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*Why ask for the moon
When we have the stars?*

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OIL & COLOUR CHEMISTRY MONOGRAPHS

Edited by R. S. Morrell, M.A., Ph.D., F.I.C.

BLACKS & PITCHES

BY

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PREFACE

IN the following pages my endeavour has been to put before the reader a concise account of our present knowledge of the black pigments and of the various bituminous materials and pitches of commerce. Whilst it may appear at a glance somewhat strange to include in one and the same volume considerations of such apparently dissimilar and unrelated classes of substances as Blacks and Pitches, a little reflection will show the arrangement to be justified. These two classes of substances are of substantial importance in a number of rather closely related Oil and Colour Industries. Moreover, in passing, it is interesting to record that the principal black pigment, carbon black, and the natural and petroleum residual asphalts are traceable to a common origin—the petroleum fields.

From those chapters dealing with the black pigments it has been thought preferable, for reasons which require no elaboration, to omit all but a mere reference to the blacks which originate in the synthetic dyestuffs industry.

The task of writing on bituminous materials and pitches is rendered somewhat difficult by reason of the confusion still existing on questions of nomenclature and classification, but without entering fully into controversy, I have outlined a scheme of classification, mainly based on that given in Abraham's well-known treatise, "Asphalts and Allied Substances."

An effort has been made to indicate as concisely as possible the results of all the most important relevant investigations of recent years and at the same time to refer briefly to current theories. Though no claim to exhaustive treatment is made in the present case, it is my hope that nothing of material importance has been omitted. Suggestions are made as to the directions in which research may usefully be undertaken, and it is hoped that the volume will prove of service to many engaged in Oil, Colour, Paint, Varnish, Ink, Rubber, and Asphalt Industries.

Every known source of information has been acknowledged in the text, but my thanks are due particularly to the Bureau of Mines, Geological Survey U.S. Department of the Interior, Washington, for the supply of several official publications and much statistical information, and for courteously permitting the reproduction of much textual matter and a number of illustrations from *Bulletin* 192, on Carbon Black. My thanks also are due to the Statistical Department of the Board of Trade for the supply of data, to Mr. C. Ainsworth Mitchell for kindly loaning the blocks

relative to Figs. 1 to 4, to Mr. A. R. Warnes for his kindness in granting permission for the reproduction of Figs. 16 to 19, to Messrs. Bennett, Sons & Shears, Limited, for the loan of the block for Fig. 20, and to the British Engineering Standards Association for authority to include several of their well-known British Standard specifications.

To the publishers my thanks are extended for useful advice and counsel and for the care taken in the preparation of the text and in the reproduction of the illustrations, whilst I am particularly indebted to the editor for much useful assistance and criticism whilst the book was in manuscript. My friend Mr. R. J. Whitaker has kindly read through some of the chapters dealing with carbon black.

Thanks are also tendered to my wife for much valuable assistance in the tedious work of compiling tables and in the preparation of the index.

For any inevitable errors of omission or commission the author alone is responsible.

H. M. LANGTON.

July, 1925.

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BLACKS AND PITCHES

CHAPTER I

INTRODUCTION

System of Classification—General Occurrence and Methods of Preparation of Black Pigments.

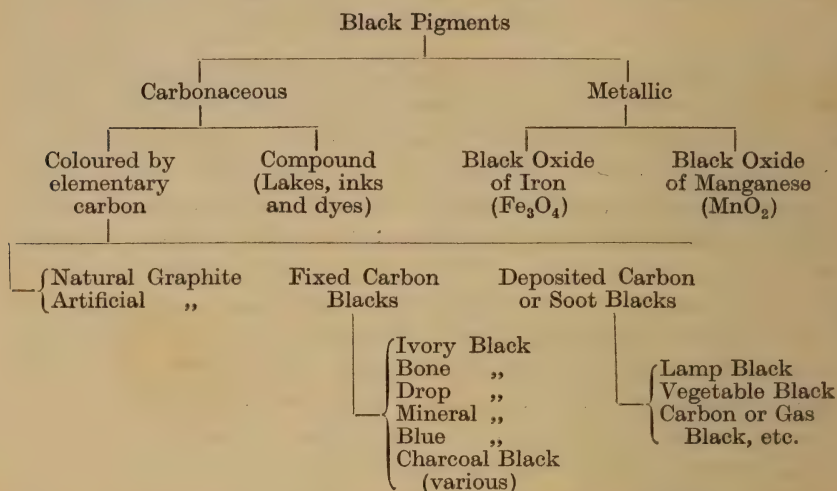
THE black pigments of commerce find use in the manufacture of black paints and varnishes, in black printing inks, in stove polishes, as compounding ingredients in manufactured rubber and in a variety of other ways. With one or two exceptions, all the black pigments contain carbon in one or other of its numerous forms as their essential colouring principle, carbon being an ideal pigment on account of its stability. It is unaffected by exposure to light or air, is resistant to acids, alkalies and other chemical agents, and suffers neither dissolution nor discoloration in contact with them or in admixture with alcohols, oils, etc. It is destroyed only at high temperature when combustion ensues. Being usually in the amorphous state, and finely divided at that, carbon pigments can be readily compounded with the usual paint and ink vehicles, giving extensive tinting and covering power, though these pigments vary considerably amongst themselves in shade and strength and in covering power. The carbon pigments can be mixed with other pigments and the usual vehicles without causing any alteration in them or being themselves altered, and as paints made from these pigments are slow in drying, such paints require more than the usual amount of driers.

A rational system of classification of the black pigments is somewhat difficult and the best is one, due to Cruickshank Smith,¹ which takes into consideration both origin and method of production (see page 14).

In this scheme of classification the term "fixed" is applied by Cruickshank Smith to those carbon blacks in which the pigment is "fixed" by an incipient coking process applied to suitable raw materials, which are carbonised in a combustion chamber to which a restricted access of air is permitted, and the pigment as produced is retained within the combustion chamber.

It will be noted from the following list that a variety of blacks containing elementary carbon exists, and unfortunately there is a lack of precision sometimes in describing them; particularly is this the case with carbon black and lampblack, it being often quite erroneously assumed that these are alternative names for

one and the same substance. Actually the various carbons and charcoals have different physical and chemical properties, they are varied in their physical structure and the uses to which they can be put. They are not identical in chemical composition nor are they pure carbon.



The deposited carbon blacks are made by one or other of the following methods, according to Roy. O. Neal²:

1. Formation by direct contact of a flame upon a depositing surface.
2. Production by combustion of an oil, tar, etc., in an inadequate supply of air, where soot is allowed to settle slowly on the floors and walls of the collecting chambers.
3. Carbonisation of solids and subsequent reduction to a state of small subdivision.
4. Production by heating carbonaceous vapours or gases to a decomposition temperature by external heating with or without air in the forming chamber. This method is usually referred to as cracking or thermal decomposition, and so far is only in the experimental stage.

Method 1 is that in use in manufacturing the typical carbon black of the American trade, whilst method 2 gives rise to the familiar lampblack whose first preparation and use are lost in the depths of antiquity. The carbonisation method, of course, leads to the production of all the familiar charcoals.

Graphite, in addition to being of natural occurrence, is also to a certain extent artificially prepared in the electric furnace.

The compound carbonaceous blacks, the lakes and dyes, of which the nigrosines may be cited as typical examples, have their genesis in the synthetic dyestuff industry.

As regards the metallic blacks, their interest, so far as they enter into the manufacture of inks and paints, is now mainly historical.

Black oxide of iron, Fe_3O_4 (or $\text{FeO}\cdot\text{Fe}_2\text{O}_3$), occurs in nature as magnetite in many parts of the world. When pure it is an iron-black substance used occasionally in some cheaper black paints and, in admixture with other blacks, in certain cheaper qualities of printing ink.

Black oxide of manganese occurs as pyrolusite (MnO_2) in Czechoslovakia, Spain, France and parts of N. America, in very pure iron-black or steel-grey, rectangular, rhombic prisms, though often as fibrous masses. Seldom is it, though, that it is found in the pure condition—more often in association with other manganese ores. When ground and finely powdered it is occasionally used as a pigment under the name of “manganese black.”

REFERENCES.

- ¹ “The Manufacture of Paint.” Scott, Greenwood and Son, 3rd edition, 1924. ² “Carbon Black,” *Bulletin* 192, U.S. Dept. of the Interior, Bureau of Mines, 1922.

CHAPTER II

GRAPHITE

Occurrence in Nature—Manufactured Graphite—General Properties and Uses in Manufacture of Lead Pencils and Graphite Paints.

GRAPHITE, known also as plumbago and blacklead, is a form of carbon which occurs as a mineral widely distributed throughout the world, generally in compact crystalline masses, but sometimes in foliaceous, scaly masses and even sometimes in a fibrous form, the variations being somewhat dependent on the locality. The production for the past few years is given in the following table ³ :—

TABLE I.
Production of Graphite (Metric tons).

	1921.	1920.	1913.
Germany	30,000	20,487	12,057
United States	2,346	8,627	4,332
Canada	367	2,020	1,961
Mexico	3,088	3,319	4,023
Austria and Styria	10,800	11,543	17,282
Bohemia and Mähren	8,500	15,000	32,175
Italy	3,000	4,190	11,145
Ceylon	4,422	9,352	28,996
Japan	950	1,135	667
Korea	11,000	14,000	14,543
Madagascar	—	4,000	7,997
Other countries	—	—	1,320
Total	85,000	100,000	136,498

In England, graphite was found at Borrowdale in Cumberland as far back as 1560, but the supply is practically exhausted there.⁴ The best qualities are now found in Ceylon, whereas the poorer qualities occur in Sweden and Bavaria, the ash in specimens from these sources being sometimes 40—60%. In the U.S. the quantities are often insufficient to make it worth while to work them in some localities.

Graphite is velvety-black or steel-grey in colour with metallic lustre, is opaque, quite soft to the touch, and makes a grey mark on paper. It crystallises in small hexagonal plates, though it also occurs amorphous, and it is then sometimes difficult to distinguish sharply between graphite and the usual amorphous charcoal forms of carbon. The specific gravity varies from 2·25 to 2·35 when pure. The principal impurities with which it is found in association are ferric oxide, alumina, silica and lime, the carbon being present to

the extent of 75—92%. For purification it is crushed and levigated and subsequently the ash content reduced by chemical treatment.

A certain amount of graphite is now manufactured by the International Acheson Graphite Company at Niagara Falls, U.S.A., the amount having been about 3700 tons in 1920. This manufacture is due to an observation by E. G. Acheson that carborundum at a temperature above 2000° C. is decomposed into carbon and silicon, the former being in the form of crystalline graphite. He subsequently observed that coke could be converted into graphite in the presence of much less silica than would be required to convert the whole of the carbon into silicon carbide, and he therefore concluded that the action was catalytic. It is now known that all forms of carbon can be converted into graphite under suitable conditions of temperature, though the rate at which this occurs varies greatly with conditions and with the nature of the reactants.

At present graphite is manufactured by the Acheson Company, according to H. D. K. Drew,⁵ by the following U.S. Patents: 542,982 of 1895; 568,323 of 1896; 617,979 of 1899; 645,285 of 1900; 702,758 of 1902, and 711,103 of 1903. For graphite powder a furnace similar to that favoured in carborundum manufacture is adopted.

Carborundum is used in constructing the furnace walls, the end-walls through which the electrodes pass being fixed and the others movable. The furnaces, which may be 30 ft. in length and of sectional area 18 ins. by 14 ins., contain a charge of clean anthracite in fine powder containing up to 10% ash, packed round a core of graphitised coke. Petroleum coke is used for making the best qualities of graphite. A current of 3000 amperes at 220 volts is first passed, but later, as the resistance decreases, the final current is 9000 amperes at 80 volts, the duration of the operation being about 24 hours, after which the graphite is cooled, removed, and ground in tube mills, and by air separation the fine material sifted from coarse particles.

Manufactured graphite in addition to containing 1—2% of amorphous carbon may contain up to 10% of ash, though in the case of the purest form the ash is no more than 0.2%.

A method for the rapid analysis of graphite has been described by G. B. Taylor and W. A. Selvig,⁶ but space forbids a description here.

Uses.

Natural graphite is mainly used for the manufacture of plumbago crucibles, 75% of the total supply being absorbed in this way;⁷

the remainder is accounted for by lubricants 10%, pencils 7%, foundry work 5%, paints 3%. Artificial graphite finds its use for electrodes, lubricants, paints, dry batteries and in boiler-scale preventives.

Its uses in the manufacture of crucibles, electrodes and foundry work are outside the scope of the present volume, though brief reference may be made to its use as a lubricant. Flaked graphite can be used dry in steam cylinders, and it is said to build up a surface on rough bearings; it is sometimes compounded with compound greases for heavy bearings and with lubricating oils for light bearings. Its lubricating properties in colloidal suspension have been discussed by H. L. Doyle ⁸ and a method of deflocculating graphite has been patented by E. G. Acheson.⁹ The fact that colloidal graphite is, however, very susceptible to the flocculating action of electrolytes, less than 0.1% of free fatty acids being sufficient to precipitate it, would appear almost to inhibit its use in this way.

It is well to remember in mentioning the lubricating properties of graphite that both it and the diamond are crystalline forms of the element carbon: the former soft and greasy to the touch, the latter one of the hardest substances known and in powdered form strongly abrasive, in striking contrast to the lubricating character of its graphitic allotrope. The new method of X-ray analysis has given the clue to these striking differences in the two allotropes, differences which must be accounted for by differences of molecular structure.

A full account of graphite as a lubricant is given in a memorandum on Solid Lubricants in the Report of the Lubricants Committee,¹⁰ to which the reader is referred for full information.

Graphite has no great use as an oil or varnish colour except in the manufacture of anti-corrosive paint for use on ironwork, and according to Zerr, Rübenkamp and Mayer ¹¹ is used exclusively in many parts of Europe for blackleading iron stoves, its fire-proof properties rendering it very suitable, and in the painting of sheet iron as a preventive against rust. The manufactured graphite when finely ground is similarly used as a paint. According to H. A. Gardner,¹² graphite gives a better paint coating when mixed with other pigments, such as red lead and sublimed blue lead. He points out the great tendency in graphite towards agglomeration of particles. In addition to being proof against rusting, graphite in a paint imparts immunity against the corrosive action of gaseous sulphur compounds, ammonia, the halogens and their gaseous derivatives, etc.

PHOTO-MICROGRAPHS OF PENCIL MARKINGS



FIG. 1.—Mark made by Borrowdale Graphite used for Pencil-making in 1851. Now in Geological Museum. $\times 20$.



FIG. 2.—Marks made by Faber's Pencil. Striations show sequence of lines. $\times 20$.



FIG. 3.—Marks made by Acheson Graphite Pencil. Striations show sequence of lines. $\times 20$.



FIG. 4.—Line in Drawing of 1831. Typical of old pencil markings. $\times 20$.

The most important use to which graphite is put with which we are concerned here is in the manufacture of black-lead pencils. According to Ainsworth Mitchell,⁴ the graphite of Borrowdale was used from the time of its discovery, about the year 1560, until the latter half of the nineteenth century for the manufacture of the pencils used throughout Europe. An account of the properties and uses of graphite in this connection is given by Cæsalpinus,¹³ though apparently the true nature of graphite was not known until demonstrated by Scheele in 1779.

About 1840, when the Borrowdale mine was becoming exhausted, efforts were made to utilise the accumulations of graphite dust, and a patent was taken out by Brockedon,¹⁴ according to which finely-sifted graphite was induced under great pressure into the form of compact blocks which could be sawn up in the usual way. About the middle of the last century, however, the composite pencil was coming into use, having first originated with Conté, of Paris, in 1795.

In Conté's process finely elutriated clay and graphite are mixed to a paste forced through dies in a cylinder, and the circular threads of pigment dried, heated in a covered crucible and afterwards fixed into the grooved wooden holders with which we are familiar. Since that time such developments as the incorporation of wax, lampblack, resin, etc., with the pigment have arisen.

According to Mitchell,⁴ the suitability of graphite for pencil-making depends, from a chemical aspect, on : (1) the proportion of carbon, (2) the amount of silicates, (3) the iron. Moreover, the physical nature of the carbon in the graphite appears to be of importance, and this is borne out by microscopical examination of marks produced on paper by graphite. In the microscopical examination, both vertical and horizontal lines are recommended by this author to be examined, using a 1 in. objective and with a strong side light. Under these conditions, in the case of Borrowdale graphite, the vertical lines show relatively few straight striations, and when these occur in the heavier strokes they are disjointed and irregular.

Table II gives the results of some analyses of graphite due to Mitchell,⁴ by whose courtesy also it is possible to reproduce the photomicrographs he prepared.

For an account of the method of analysing pencil pigments the reader must consult the original paper.

Marks made by pure graphite, when examined under the microscope in a vertical position with illumination at right angles, show

TABLE II.
*Analyses of Graphites.**

	Carbon.	Ash.	Silicates.	Iron and alumina.	Microscopical appearance of markings.
1. Borrowdale crude graphite (Banks & Co.)	% 52.99	% 47.01	% 37.68	% 10.26	Irregular deposit of pigment. Irregular striations, many following fibres of paper. Few straight lines.
2. Borrowdale graphite used in 1850 for pencil-making (Geol. Museum, Ex. 54.)	90.33	9.67	7.03	1.08	Irregular disjointed striations, some brilliantly lit up. In lighter strokes irregular striae following the fibres.
3. Borrowdale graphite	90.73	19.27	11.44	3.31	Black pigment deposit. Fibres of paper lit up, but few straight striations visible. Type of graphite common in old pencil writing and drawings.
4. Ceylon graphite	92.78	7.22	3.90	2.45	Black pigment deposit. Irregular silvery branching striations. Groups of straight disjointed striae. Brilliantly lit up in places.
5. Swedish graphite	43.84	56.16	44.09	7.61	Greyish pigment irregularly distributed. Numerous groups of disjointed straight striae, lit up in places.
6. Greenland graphite made into pencils for King of Denmark (Geol. Museum)	79.63	20.37	15.30	4.03	Rich black pigment covered with brilliant branching striae. Effect of silvery sheen. Fibres of paper lit up.
7. Canadian graphite	93.21	6.79	3.82	0.27	Black pigment on sepia grounding. Heavy strokes fairly free from striations. Here and there broad silvery streaks.
8. Siberian graphite. (Geol. Museum. Ex. 33).	77.45	22.55	17.41	0.12	Rich black pigment showing fibrous shimmer. Fine irregular disjointed striations.
9. Acheson's graphite for pen-cil-making (powder)	99.83	0.17	—	faint trace	
10. Acheson's graphite for electrodes (solid)	96.80	3.20	—	trace	Uniform silvery shimmer composed of points reflecting the light.

* In these and subsequent analyses the iron and alumina were precipitated together and were not separated. The proportion of alumina present was generally very small. The extraction with hydrochloric acid was continued until the residue gave only the faintest coloration with ferrocyanide.

irregular silvery strokes or broken striations. In the modern pencil pigments, in which clay is incorporated with the graphite, fine beaded striations parallel and uniform throughout the pencil mark appear. An examination of Figs. 1, 2, 3 and 4 enables these differences to be appreciated.

Mitchell ⁴ has also given the composition of a number of pencil pigments made by the Conté firm, reproduced below :

TABLE III.

Composition of Pigments in Conté's Pencils. Series 1020.

Pencil no.	Graphitic carbon.	Loss at 200–210° C.		Silicates.	Iron oxide with traces of Al_2O_3 .	Remarks.
		Wax, etc.	Ash.			
	%	%	%	%	%	
0	60.28	12.85	26.87	23.70	2.07	Puce-coloured ash
1	55.43	17.71	26.86	16.54	5.93	"
2	57.63	13.76	28.61	25.61	1.90	"
3	50.80	10.60	38.60	34.95	0.28	"
4	48.52	12.21	39.27	34.98	3.79	"
5	36.06	8.41	55.53	36.29	5.35	Titanium present

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CHAPTER III

THE FIXED CARBON BLACKS

Bone Blacks, Wood Charcoals and Mineral Blacks—Mode of Preparation—Properties.

THE basis on which the blacks, described in this chapter, are differentiated from other black pigments has been mentioned along with their general method of preparation in the introductory chapter. Leaving out of consideration the mineral blacks, the “fixed” carbon blacks are known perhaps more familiarly as the charcoal blacks, and they all have the same genesis. When non-volatile carbonaceous substances are heated in closed retorts or kilns out of contact with air, such substances undergo decomposition, and water, certain volatile carbon compounds, such as carbon dioxide, carbon monoxide, acetic acid, acetone, hydrocarbons, and certain oily, tarry or resinous compounds result, and a residue of elementary carbon, associated with a greater or lesser amount of mineral ash, remains behind in the retort. The amount and nature of such elementary carbon or charcoal remaining depend on the nature of the raw material, the type of plant used, the temperature at which the operation is carried out and the extent to which volatile decomposition products are removed from the sphere of action. This method of producing charcoal blacks is termed dry distillation.

A convenient subdivision or classification of the black pigments to be reviewed here is the following :

- (a) Bone Blacks, including ivory black and drop black.
- (b) Wood Charcoals, including vegetable charcoals and vine black.
- (c) Mineral Blacks.

This subdivision serves to indicate the origin of the black, and to some extent is further justified by some of the characteristics exhibited by these various blacks.

(a) *Bone Blacks*.—These are made by calcining bones in airtight retorts, the bones being previously freed from adhering fat and ground to a coarse powder and sifted. During calcination, when black for pigment is the primary need, the products of combustion are burned instead of being recovered, the claim being that a better product results, but this is purely conjectural. At any rate, the bone black so prepared has greater colour-strength and better working qualities than sugar-house black, where, during the calcination, the by-products of the dry distillation are suitably recovered, and the black is obtained in a granular form. After

being used in sugar filtering, it is washed, ground wet, dried and afterwards finds use as a paint pigment under the name of Drop Black.

If bone black be treated with acid and the calcium salts dissolved, a finely-grained carbon almost free from ash results. Acid-washed black has a very deep black colour, and in consequence of its fine state of division a great deal of colour-strength.

Ivory black is a form of bone black made, not, as formerly, by charring the waste cuttings of ivory, but by the dry distillation of the best quality of bones obtainable after defatting, etc. Ivory black is more intense in blackness than the average quality of bone black.

A very important use for bone black is as a decolorising agent and deodorant in the filtering of sugar and other solutions and oils; although it is outside the scope of the present volume to discuss the utility of bone black in this direction, reference may be made to the recent work of P. M. Horton¹⁵ and W. D. Horne,¹⁶ on the rôle played by bone black (or animal charcoal, as it is sometimes termed) in decolorising. It is interesting to note, however, according to Oliver Wilkins,¹⁷ that much of the bone black used as a pigment comes second-hand to the colour manufacturer from the sugar refiner. The "spent" animal charcoal of the latter is thoroughly washed and ground by heavy stones to reduce the spongy, carbonaceous matter to a fine, silky powder. According to this author, the old custom was to sell this black in lumps made by dropping the black paste, as it came from the levigating stones, in little heaps on to boards for drying, and the following out of this prescribed ritual and the production of the black in peculiarly shaped pieces was a criterion of purity. To some extent even to-day this procedure has to be adopted in order to satisfy those users who are unconvinced of the purity of finely-ground bone black sold in the form of a powder.

Generally speaking, the various bone blacks are denser than carbon and lampblacks. They are of bluish-black colour, have a specific gravity of 2.6 to 2.80 usually, and are characterised by a high content of ash, often as high as 80% or upwards, with a correspondingly low carbon content, which may be as low as 10%, the ash being largely calcium phosphate.

(b) *Wood Charcoals*.—The old-fashioned method was to carbonise wood in heaps, taking care that access of air was very restricted, but the method had many disadvantages, and owing to lack of proper control of air supply, temperature, etc., it was impossible to manufacture a product of uniform composition and of guaranteed

purity. Ultimately, therefore, the method of heating in retorts or air-tight crucibles was resorted to, as in the manufacture of bone black.

The subject has been reviewed by T. W. Pritchard,¹⁸ who refers to the old destructive distillation process carried on in a series of retorts fitted with condensers set in brickwork, under which was a furnace. Temperature control is an important feature of the operation. This process gave a high yield of products.

Later, the process of subjecting to steam distillation wood rich in resins and turpentine was resorted to before commencing carbonisation.

A modern process, followed in the United States, and termed the solvent process, is to take pine wood, which is shredded and then extracted by means of solvent naphtha, which removes in good yield the turpentine and resins, which are recovered after removal of the solvent. Subsequently the extracted wood is carbonised.

The yield of charcoal from wood depends, of course, on the nature of the wood carbonised and on the way it is heated. G. Martin⁵ has given some statistics illustrative in this connection of the yield of charcoal from air-dried wood, viz. :—

TABLE IV.
Yield of Charcoal from Air-dried Wood.

Nature of wood.	Charcoal yield %.
Beech slowly heated	26·7
„ quickly „	21·9
Oak slowly heated	34·7
„ quickly „	27·7
Birch slowly heated	29·2
„ quickly „	21·5
Pine slowly heated	30·3
„ quickly „	24·2

Besides the resinous woods, such materials as sawdust, coconut shells, cork cuttings, beech twigs and leaves and similar vegetable matter are carbonised, particularly for the production of vegetable charcoal, though for the true vine black, now largely of historic interest, vine twigs, grape husks and washed wine lees are carbonised.

The apparent specific gravity of the various charcoal blacks varies from 0·106 to 0·206, but when air-free they have a real specific gravity of about 1·8. With the exception of vine black, none of them has any great colour-strength, though they are used mixed with other black pigments.

In the table given below are the results of analyses of a number of bone, wood and other charcoals examined in the author's laboratory ^{18a} during the past four years.

TABLE V.
Results of Analyses of Various Charcoals.

Material.	Moisture.	Ash.	Volatile matter.	Fixed carbon.
	%	%	%	%
Bone black I	2.88	66.40	10.82	19.90
Bone black II	3.35	78.52	8.86	9.27
Vegetable charcoal I	3.70	3.35	6.70	86.25
" " II	6.57	3.40	6.78	83.25
" " III	6.49	4.42	10.71	78.38
" " IV	5.30	4.50	9.28	80.92
Willow charcoal	3.26	2.10	13.66	80.98

With the exception of the bone blacks, none of the above was of intense black colour. The bone blacks were high in ash content and their texture was not so fine as that of the other blacks recorded above. Some of the vegetable charcoals were particularly fine, having almost the fluffy texture of a typical American carbon black.

(c) *Mineral Black*.—This is a black pigment made by grinding a black form of slate or clay shale which has a carbon content of about 30%. This shale exists widely distributed, occurring in a specially pure state in Spain, less so in Switzerland, the Tyrol and Italy, and is generally blue-black to brownish-black in tint.

Certain so-called mineral blacks are also produced, similar to the above in character, by carbonising in retorts waste coal dust and Scotch boghead mineral, the charred mass containing up to 30–40% of carbon.

According to Gardner,¹² mineral black, owing to its low carbon content, has only a low tinting power, though it finds use as an inert pigment in compounded paints. It has a flocculent appearance, the particles showing a strong tendency to mass.

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CHAPTER IV

CARBON BLACK

Its Manufacture from the Natural Gas of Petroleum Fields—Statistics—Theory of its Formation—Commercial Methods of Manufacture by the Channel Process, Rotating Disc Process, Plate Process, Roller Process and by Thermal Decomposition—Attempts at Alternative Methods of Production—General Properties and Analyses—Methods of Testing—Uses of the Pigment.

CARBON black is the fluffy, velvety-black pigment produced in the form of an impalpable powder by the burning of natural gas against a metal surface. This black is not to be confused with lampblack, from which it differs in several respects, and which is made by entirely different methods. According to G. L. Cabot,¹⁹ who is one of the pioneers of the American carbon black industry, certain printing-ink makers of New York and Philadelphia found that the soot, deposited by the suitable burning of artificial gas, gave a beautiful gloss and an intense tint to printer's ink, differing in both these respects from the older and more familiar lampblack.

The first recorded use of natural gas for lighting purposes in the U.S.A. occurred as far back as 1826 in New York State, but it was only in 1872 that its general use for domestic purposes came about, the gas being conveyed along pipes from the gas wells of the petroleum fields. The same year saw the erection at New Cumberland of the first factory to manufacture carbon black on a commercial scale.² In this factory gas from a gas-holder passed through pipes to gas-jets arranged in the same horizontal plane beneath slabs of soapstone that were pierced with numerous orifices, through which excess smoke and waste gases passed. Over the slabs was a roof provided with dampers for controlling ventilation. Transverse horizontal scrapers below the slabs were supported, and moved in horizontal grooves in the lower and opposite sides of the roof, the scrapers from time to time removing the carbon black deposited by the burning of the gas. The carbon black fell into sheet-iron troughs suitably supported. The depositing surface was kept cool by an arrangement dependent on continuously circulating water.

The first lot of 500 lbs. of carbon black marketed sold for \$2.50 per lb., but by 1881 the price had fallen considerably, and the movement in the selling price since then is indicated by the chart ² (Fig. 5). Whereas the total production in 1881 was probably only 400,000 to 500,000 lbs., by 1920 it had risen to about 50,000,000 lbs.

Since the early establishment of the carbon black industry

numerous innovations have been introduced and considerable advances made in the methods of manufacture. The extent and

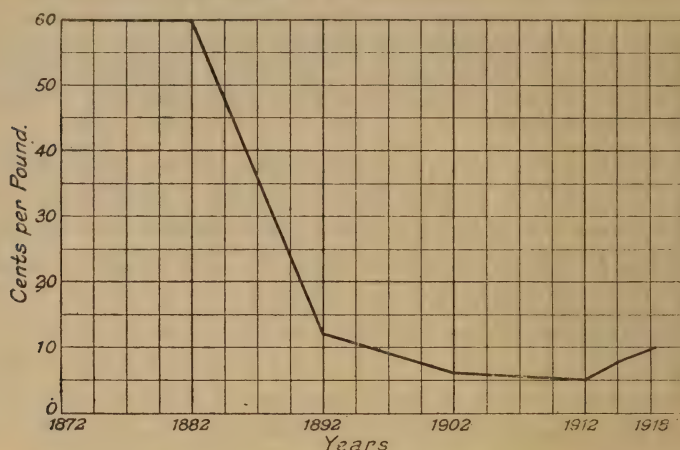


FIG. 5.—Selling Price of Carbon Black.

value of the industry are best gathered from the following table, due to E. G. Sievers ²⁰ :

TABLE VI.
Carbon Black Produced from Natural Gas.

State.	No. of plants.	Quantity produced (lbs.)	Value \$.	Average price per lb. (cents.)	Average yield of carbon black per 1000 c. ft. (lbs.)	Quantity of gas used 1000 c. ft.
1919						
West Virginia ...	23	29,925,614	2,358,119	7.9	1.3	23,117,332
Louisiana	7	14,024,606	933,334	6.7	0.7	20,291,021
Wyoming	2	4,868,947	231,747	4.8	1.1	4,306,153
Montana						
Oklahoma	2	2,922,274	244,726	8.4	1.5	1,954,029
Kentucky						
Pennsylvania ...	2	315,500	48,114	15.3	1.4	227,700
	36	52,056,941	3,816,040	7.3	1.04	49,896,235
1920						
West Virginia ...	19	26,659,469	2,221,674	8.3	1.43	18,628,780
Louisiana	15	18,565,498	1,455,764	7.8	1.0	18,099,800
Wyoming	1	5,850,313	326,424	5.6	1.6	3,673,108
Montana	1					
Kentucky	1					
Pennsylvania ...	2	246,612	28,424	11.5	1.2	197,290
	39	51,321,892	4,032,286	7.9	1.26	40,598,978

The variation in the average yield of carbon black per 1000 c. ft. of gas burned is indicated in these figures. It must be remembered that there are considerable variations in the price of gas in the different fields. The industry is necessarily a migratory one—gas may become prohibitive in price in a particular district or the supply may become intermittent or fail altogether.

In selecting the location of a plant, an idea of the ultimate supply of gas available should be obtained by reference to rock pressure, thickness of gas-bearing strata, porosity of the sands, the presence or absence of intruding waters, and some knowledge of the previous history of the field and of the drilling which has been practised. The following summary, due to R. O. Neal,²¹ is useful in this connection :

“When planning the construction of a carbon-black plant, information on the following points should be obtained; distance from railroad or navigable stream, depth of wells, thickness of gas-bearing strata, gas pressure, gasoline content and knowledge as to whether gas is casing-head or dry, amount of proven territory, history of field, drilling practice, location of field in regard to large centres for domestic and industrial distribution of gas, distance from large trunk pipe-lines for transportation of gas, open flow capacity of gas wells on prospective leases, and a test on the richness of gas for the approximate quantity of carbon black that one expects to procure per thousand cubic feet.”

It is important to test natural gas for its carbon-black value both by chemical analysis and by means of special test apparatus in which a known quantity of the gas is burned and the carbon black deposited on a metal plate, collected and weighed.^{22, 23} The variation in the amount of carbon black obtained from different qualities of gas burned by the same process is given in Table VII, due to D. B. Dow.²

It will be observed that the yield of carbon black from natural gases follows very closely the ethane content, the heating value of the gas and its content of elementary carbon calculated from the hydrocarbons as determined by analysis. Methane (CH_4) contains 33.5 lbs. of carbon per 1000 c. ft., as against a content for ethane (C_2H_6) of 67 lbs. per 1000 c. ft., and the bearing of this is seen in the yield of carbon black obtained in the case of Wyoming natural gas.

Theory of Formation of Carbon Black.

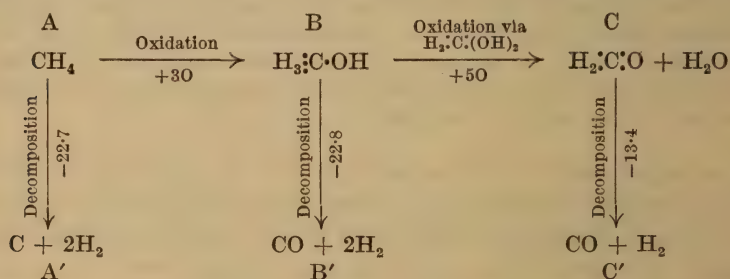
The burning of natural gas in an incomplete supply of air results in the liberation of carbon, and the combustion, contends Bone,²⁴

TABLE VII.

Carbon Content and Quantity of Carbon Black Recovered from Natural Gas.

	Louisiana.	West Virginia.		Wyoming.
	A.	B.	C.	D.
Methane per cent.	94.12	70.75	65.23	46.45
Ethane „	3.44	24.14	30.07	43.10
Carbon dioxide „	0.50	0.28	1.56	0.96
Nitrogen „	1.94	4.83	3.14	9.49
Net heating value in B.Th.U. per c. ft. at 0° C. and 760 mm. pressure in lbs.	962	1,086	1,134	1,176
Carbon per 1000 c. ft. of gas calculated from carbon content of methane and ethane ... in lbs.	33.8	39.9	42.3	44.3
Carbon black per 1000 c. ft. of gas reported obtained in lbs.	0.80	1.00	1.10	1.40
Percentage recovery	2.4	2.5	2.6	3.1

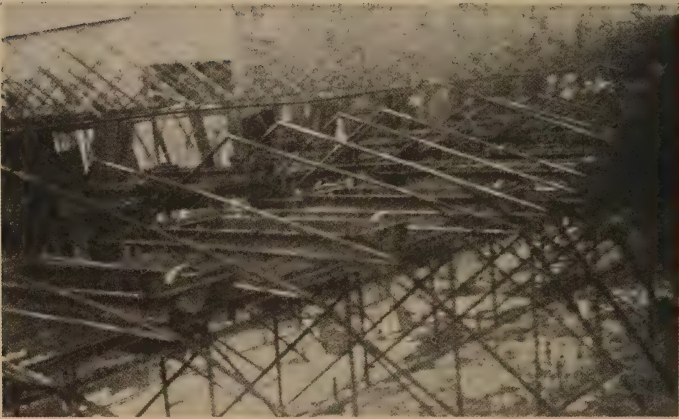
takes place according to the following scheme as a result of hydroxylation :



The tendency is always to pass from A to C. When the proportion of methane to oxygen is that which is expressed by $\text{CH}_4 + \text{O}_2$, the reaction passes from A to B to C to C'. If the ratio is $2\text{CH}_4 + \text{O}_2$ or higher even, then only a part of the methane can be oxidised through the reaction A to C, and so part is decomposed at A by the heat evolved in the A to C reaction. The minimum amount of oxygen in which a methane flame will burn is 15.6%. Only in the inner part of the flame, where oxygen supply is low but where the heat is sufficient to decompose the methane, will carbon be evolved, and the percentage of carbon to be obtained by the incomplete combustion of methane is low; gases rich in ethane and its higher homologues give higher yields of carbon. Bone noted that the decomposition of methane, in the explosive combustion of hydrocarbons, was a surface effect leading to a hard, gritty carbon, whilst



A



B

FIG. 6.—Channel Plant in course of Construction.

the decomposition of ethane, ethylene, etc., took place throughout the whole mass of the gas and yielded a soft carbon. The decomposition of methane and the influence of different surfaces on this have been discussed by W. E. Slater.²⁵

The function of the cold metallic surface, which is a feature of all the commercial processes for making carbon black, is to cool the liberated carbon in the flame sufficiently to prevent its combustion, but obviously an optimum temperature is necessary. Too cold a surface may prevent the maximum separation of carbon—too hot a surface will cause too much carbon to be burnt and may even change the physical characters of the carbon remaining. In this connection a carefully regulated air supply is possibly the chief desideratum, whilst the best temperature is about 500° C.

Commercial Methods of Manufacture.

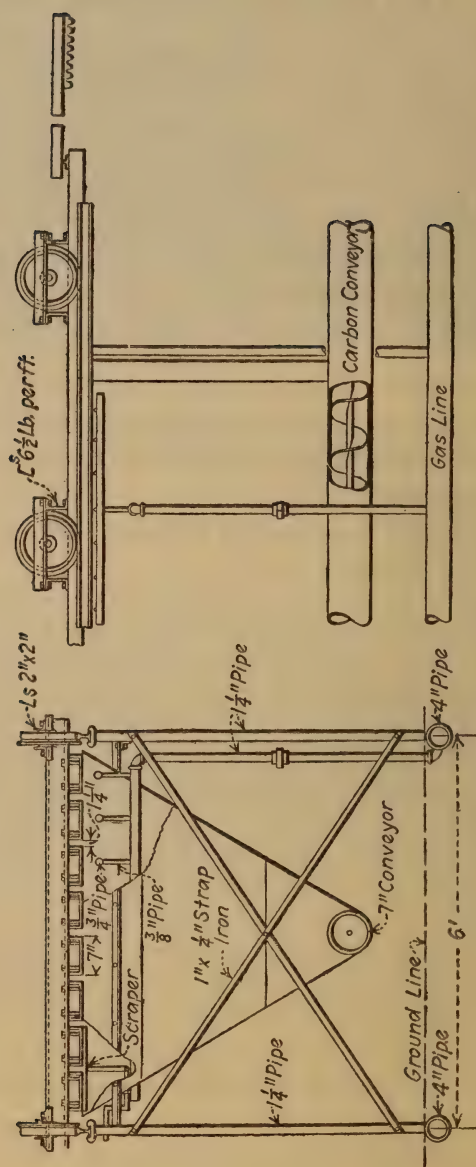
The principal methods in commercial practice in U.S.A. are the following, arranged according to the quantity of black produced :

1. Channel process.
2. Small rotating disc process invented by A. R. Blood in 1888 and now extensively used.
3. The large plate process invented by G. L. Cabot.
4. The roller process invented by E. R. Blood.
5. Thermal decomposition or cracking. (This is still largely in the experimental stage.)

The Channel Process.—Briefly this is operated as follows, according to R. O. Neal, who has described the process in detail in the *Bulletin*.²

The natural gas from the wells, after suitable pressure regulation, passes through gasometers, which regulate the flow of gas, and pass it on to burners arranged in the condensing buildings. It is essential that equal gas distribution be obtained in each building. The condensing buildings are of sheet iron, about 700 ft. long and 8 to 10 ft. in width, arranged in rows along both sides of an alley, through the centre of which alley and placed at right angles to the condenser units is the main driving shaft operating the machinery within the units.

In the interior of the buildings are trestles or tables about 6 ft. wide and about 6 ft. high, and on each trestle are usually placed 8 rows of channels, these latter being hung from trucks that run on overhead rails. The channels have a reciprocating motion of 4 to 5 ft.



In Fig. 6 (A and B), taken from *Bulletin* 192 of the Bureau of Mines, U.S. Department of the Interior, Washington, and reproduced here by the courtesy of that Department, particulars of a channel plant in course of construction are shown.

The gas is burned through lava tip burners, there being usually 1600 of such in a building of the size described here. An even, luminous, smoky flame results, the draught being suitably regulated, and the carbon black is deposited on the underside of each channel. Underneath the channels are arranged the carbon-collecting hoppers, spaced about 4 ft. apart, and these catch the carbon removed by scrapers set in the hoppers; different types of scrapers with different methods of actuating them are in use, but one type in use is that shown in Fig. 7, reproduced from *Bulletin* 192.

The carbon black is conveyed by spiral conveyors to a room containing bolting machines; these are galvanised sheet-iron drums having across one end a screen of 45- to 60-mesh iron, over which fibre brushes rotate in order to remove grit and scale from the black. From the bolters, the black is conveyed to a storage bin, and packed in $12\frac{1}{2}$ lb. sacks, or in 150 lb. ones if for export.

Plants are usually built in 60 barrel units (50 lbs. black per barrel), and there are generally 18 buildings to an installation. A 20—25 h.p. internal combustion gas or expansion engine is quite sufficient to actuate the channels and other moving parts of an installation.

A detailed plan of a carbon-black plant is shown in Fig. 8, reproduced from the *Bulletin*.

Small Rotating Disc Process.—In this process, invented by A. R. Blood ²⁶ in 1888, and now in extensive use, the gas is burned at lava tips set to the number of 18 to 24 in the upper side of a ring of about 28 ins. diameter. The carbon black is deposited on cast-iron discs as shown in Fig. 9, reproduced from the *Bulletin*.

The discs are 36—42 ins. in diameter, and together with the driving gear and pinion resemble flat umbrellas. The hopper and the scraper radiate from the shaft and, like the burners, are stationary. The discs are arranged in rows of 21 each, with 4 rows to the condensing building, and an independent driving shaft for each row of discs. One unit plant has usually 16 to 20 buildings.

In all other respects the methods detailed in the channel process are followed.

The Plate Process.—This was invented by G. L. Cabot ²⁷ about 1892, and the details of the process are shown in Fig. 10, reproduced from the *Bulletin*.

The plates on which the carbon black is deposited are 24 ft. in



FIG. 9.—Depositing Surface for Carbon in the Rotating-Disc Process.

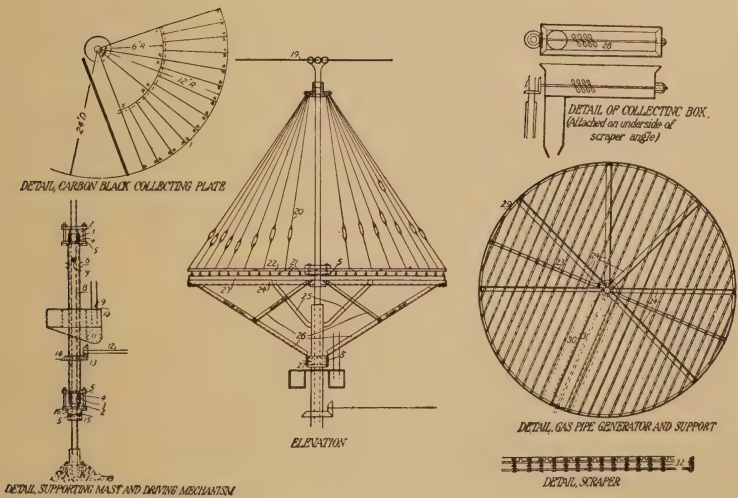


FIG. 10.—Details of the Plate or Cabot Process.

about 24 to 32 hoods, and a like number of hoppers. The buildings are usually 65 to 100 ft. long and 25 to 35 ft. in width.

Fig. 11, reproduced from the *Bulletin*, shows the details of this system.

Various factors, such as the design of the plant, weather conditions, gas pressure and the presence of salt water or oil in the gas, affect the yield of carbon black obtained in the commercial methods of manufacture outlined. Nothing apparently is to be gained by the artificial cooling, using air or water, of the cooling or depositing surfaces of carbon-black plants.

For a discussion of the economics of the industry the reader is referred to the *Bulletin* and to papers mentioned in the bibliography at the end of this chapter.

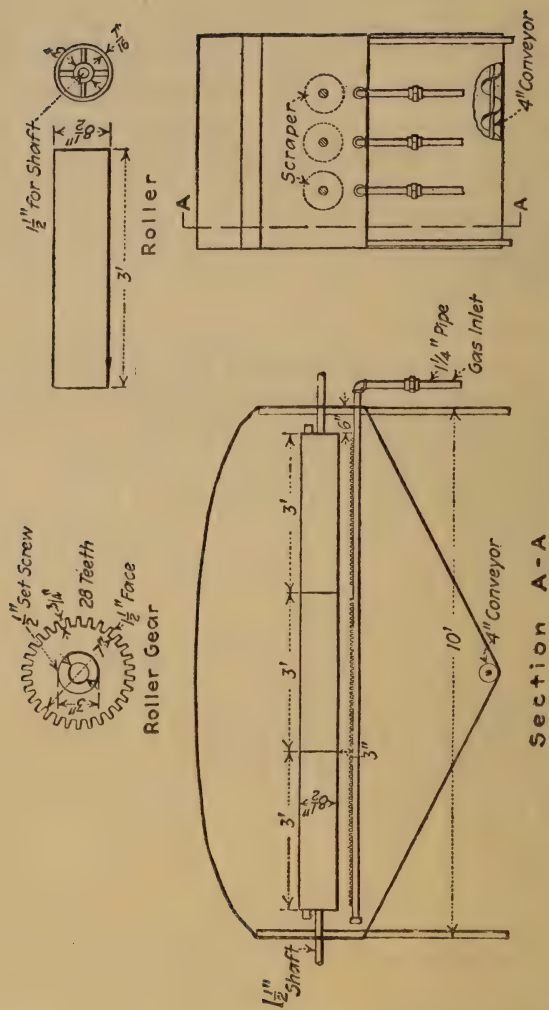
Other Methods of making Carbon Black.

Carbon black was first manufactured from artificial gas, and, as R. Irvine ²⁹ pointed out many years ago, was made in this country long before American natural gas was so used.

The same quality of black was made with similar but smaller apparatus, ordinary town gas being used as far back as 1860. To produce 1 lb. of black required 1000 c. ft. of gas, and the cost was 5s. per lb. of black obtained. Irvine ²⁹ suggested that gas from the Scottish shale retorts might be used.

One firm in this country is manufacturing carbon black from coke-oven gas, but beyond the fact that black is generally equal in quality to the American carbon black, no information is available. It would be interesting to know the yield of black from 1000 c. ft. of this gas, in view of the fact that in the case of natural gas the yield of black bears a close relationship to the ethane content of this gas. P. Lebeau and A. Damiens ³⁰ have given the composition of a number of samples of coke-oven gas, the ethane content being only 0.45 to 1.64%, which is very much lower than the recorded figure for any natural gas, and it seems legitimate to infer therefore that the yield of carbon black from coke-oven gas is much inferior to that from any natural gas.

Acetylene black has been made by exploding mixtures of acetylene and air under pressure, the acetylene being made from the refuse of calcium carbide factories. Patents ^{31, 32, 33, 34} have been effected from time to time describing the manufacture of acetylene black, and according to G. L. Cabot ³⁵ acetylene gas possesses the quality of exploding by itself, without admixture, and black has been made by exploding this gas under 5 atmospheres pressure, either by compression or by electric spark. In those cases where



Section A-A

FIG. 11.—The Roller or Rotating Cylinder System.

explosion occurs in the presence of air, it has been shown that the acetylene not only is oxidised, but is actually dissociated. The black obtained is inferior in colour and strength to the carbon black from natural gas, but is useful where its bluish tinge gives it a preference in certain industries. The supply is, however, uncertain, and is chiefly confined to the continent of Europe.

The yield, in the case of a small Chicago plant burning acetylene, as in the manufacture of carbon black from natural gas, is 11.6 lbs. of black per 1000 c. ft. of acetylene—a recovery of 17.3%.

Numerous other methods have been patented for producing a high yield of carbon from natural gas or other hydrocarbons, the gas being generally split up into carbon and hydrogen in a retort at high temperature in contact with refractory material. Mention may be made in this connection of the work of R. H. Brownlee and R. H. Uhlinger,³⁶ of Szarvasy,³⁷ of McCourt and Ellis,³⁸ of W. G. Laird,³⁹ and of a recent attempt of J. A. McGuire,⁴⁰ who causes chlorine to react with an excess of hydrocarbon. No great quantities of usable carbon black have been made by any of these processes.

Properties of Carbon Blacks.

All the carbon blacks are very intense in colour, glossy, whether rubbed dry or in varnish, and have an extraordinary mixing strength. They mix with water by simply shaking them with it, though lamp-black usually will not, and this is a convenient method of distinction.

Carbon blacks generally are hygroscopic, and some blacks will absorb as much as 15% of moisture. Carbon black contains considerable quantities of carbon monoxide, carbon dioxide and oxygen, the latter probably being present in some sort of loose combination as "fixed oxygen," and the carbon dioxide may be present to an extent equal to 1% of the weight of moisture present.

The specific gravity of carbon black varies from 1.8 to 2.1, and its determination requires some little care in order to eliminate the air bubbles always enclosed in the pigment. The determination may be carried out in the usual type of specific gravity bottle, which is weighed empty, full of distilled water and then full of the dry pigment. The bottle containing the pigment is then filled with distilled water and the enclosed air bubbles are removed by heating and until the pigment is thoroughly wetted. The bottle and contents are then brought to a temperature of 15.5° C., and additional water is added if necessary, until the bottle is quite full, and then weighed again. The ratio of the weight of the pigment to the weight of water displaced by it gives the true specific gravity of the pigment.

When making this determination for lampblack, it is preferable to use benzol or some liquid which will completely wet the pigment. Gardner ⁴¹ has drawn attention to the difficulties to be encountered in determining the specific gravity of fine pigments and indicated how these difficulties may be overcome.

The present writer ⁴² has examined a number of genuine carbon blacks, with the results recorded below :

TABLE VIII.
Analyses of Carbon Blacks.

Proximate analysis.	Long black No. 1.	Long black No. 2.	Short black No. 1.	Short black No. 2.
	%	%	%	%
Moisture	3.78	5.58	2.16	3.25
Volatile matter	10.68	10.00	4.68	5.68
Fixed carbon	85.44	84.40	93.11	91.02
Ash	0.10	0.02	0.05	0.05
True specific gravity	1.88	1.85	1.79	1.80

The acetone extract of the above blacks was a mere trace—too small to record in the data.

The volatile impurities in carbon black may be removed, according to J. C. Morrell,⁴³ by heating the black to 450—600° C. in an iron crucible under suitable conditions.

In Table IX. are details of some very complete analyses of carbon blacks due to W. A. Selvig.

The determination of volatile matter is carried out in the same way as outlined in any of the well-known volumes dealing with the analysis of fuel, and need not be detailed here. The U.S. Bureau of Mines recommends for the determination of moisture, ash, and acetone extract the following standard methods, full details of which will be found elsewhere, due to F. M. Stanton and A. C. Fieldner.⁴⁴

Moisture.—"A one-gram sample of the black is placed in a weighed porcelain crucible, and heated for 1 hour at 105° C. in a constant temperature oven in circulating dry air. The crucible is then removed from the oven, covered, and cooled in a desiccator over sulphuric acid. The loss in weight multiplied by 100 is recorded as the percentage of moisture."

Ash.—"The crucible containing the residue from the moisture determination is heated gradually with a Meker burner, or better in a muffle furnace, to about 750° C. or to a cherry-red. Ignition is continued until all the particles of carbon have disappeared. The

crucible is then cooled in a desiccator and weighed, after which it is heated again for 15 minutes, cooled in a desiccator, and re-weighed. If the change in weight is more than 0.0002 gram, the process is repeated, until successive weighings are constant to this figure. The weight of the crucible and ash minus the weight of the crucible is taken as the weight of the ash."

TABLE IX.
Analyses of Carbon Blacks, Lampblacks and other Blacks (Selvig).

Brand	Manufacturer	Method of manufacture	Lab- oratory No.	Con- diti- on	Proximate				Ultimate				Calorific value.			
					Mois- ture	Volu- tile matter	Fixed carbon	Ash	Hy- dro- gen	Car- bon	Nitro- gen	Oxy- gen	Sul- phur	Calo- ries	B. t. u.	Real speci- fic grav- ity
D E carbon black	G. L. Cabot	24-foot plates, large burners, Granville, W. Va.	31322	1	2.76	10.79	86.64	0.11	1.02	91.97	0.02	6.96	0.02	7,578	13,640
P N Elf carbon black	do.	3-foot plates, large burners, Spencer, W. Va.	22984	2	2.38	8.59	91.41	0.07	1.17	92.29	0.02	6.97	0.01	7,798	14,027
New Vulcan carbon black	do.	3-foot plates, average size lava tips, Granville, W. Va.	22980	2	3.12	3.56	91.22	0.08	1.05	93.63	0.03	5.19	0.00	7,562	13,666	1.74
Monarch carbon black	do.	3-foot plates, average size lava tips, Glasgow, W. Va.	32379	2	2.94	2.76	94.09	0.08	1.02	96.64	0.06	2.51	0.00	7,897	14,215	1.78
Kalstra carbon black	do.	Cylindrical rollers, cylindrical tips, Glasgow, W. Va.	32381	2	2.94	6.31	93.69	0.09	1.03	95.13	0.08	4.22	0.02	7,778	13,673	1.68
Auk carbon black	do.	Channels, medium size lava tips, Glasgow, W. Va.	32383	2	2.64	10.40	84.16	0.14	1.11	87.89	0.08	10.68	0.01	7,106	12,791	1.88
Long carbon black	do.	Probably cylindrical roller sys- tem, Glasgow, W. Va.	32386	2	7.13	7.25	92.75	0.02	1.37	94.56	0.04	4.31	0.00	7,773	13,965	1.55
Short carbon black	do.	Probably channel or 3-foot disk tips, Glasgow, W. Va.	32385	2	3.02	5.48	91.47	0.03	1.08	93.50	0.04	5.26	0.00	7,618	13,712	1.78
Rubber carbon black	do.	Unknown	32387	2	3.02	5.48	91.47	0.03	1.08	93.50	0.04	5.26	0.00	7,618	13,712	1.78
No. 54 carbon black	do.	Unknown	31884	2	2.48	8.07	89.43	0.02	0.99	92.74	0.03	6.26	0.02	7,660	13,788	1.61
Sample from a rub- ber company car- bon black	do.	Unknown	31885	2	2.74	7.41	91.43	0.02	1.08	93.50	0.04	5.26	0.00	7,618	13,712	1.62
Triangle carbon black	Eastern Carbon Co.	3-foot disks, Shreveport and Burren Creek, W. Va.	32008	1	2.25	5.73	94.25	0.02	0.74	94.78	0.01	4.37	0.00	7,795	13,871	1.67
Full-seve carbon black	do.	Unknown	32007	1	3.56	5.73	94.25	0.05	1.19	98.17	0.04	10.54	0.01	7,212	12,982	1.60
Geraintown lamp- black	Patton Co.	Incomplete combustion of oil, probably "dead oil"	32247	2	3.39	2.56	97.35	0.00	0.53	97.62	0.11	1.18	0.00	7,698	14,276	1.70
Lampblack	Binney & Smith	do.	31983	2	3.12	17.84	82.01	0.00	1.20	90.87	0.09	7.41	0.00	7,029	13,723
Do.	L. Martin Co.	do.	32548	1	2.67	14.06	92.77	0.10	1.76	98.94	0.10	8.84	0.00	7,484	13,471
Black from crack- ing natural gas	do.	Heated, reagent, Carbo-Hydro- gen Co., Coraopolis, Pa.	32545	2	1.02	7.8	92.87	0.00	1.00	98.19	0.10	6.30	0.00	7,673	13,511
By turning pure gas into a hot surface combustion furnace	do.	do.	32546	2	1.25	6.40	92.11	0.24	1.29	98.78	0.01	1.61	0.00	7,850	14,310	1.72
Bone black	Binney & Smith	do.	31985	2	3.04	10.93	90.28	0.03	0.83	97.49	0.08	5.31	0.00	7,465	14,168
Vine black	do.	do.	31987	2	3.38	80.26	18.72	0.00	3.22	63.53	7.77	24.98	0.42	4,912	8,842
Willow charcoal	do.	do.	31988	2	4.18	23.67	40.79	0.00	3.82	51.02	8.89	17.58	0.38	4,017	6,742	1.02
Wood-pulp black	do.	do.	31989	2	3.24	12.05	82.23	0.07	1.88	73.74	1.14	22.69	0.45	5,824	10,438
do.	do.	do.	31990	2	3.45	15.45	84.55	0.00	2.31	99.62	0.00	17.62	0.08	7,019	14,254
do.	do.	do.	31991	2	6.42	6.78	78.94	0.00	1.60	83.20	0.17	9.69	0.48	6,973	12,561
do.	do.	do.	31992	2	11.04	88.06	1.00	0.00	1.00	88.00	0.00	1.00	0.00	7,886	14,162

a The form of analysis is denoted by number as follows: 1—sample as received; 2—dried at a temperature of 105° C.; 3—moisture and ash free.

Acetone Extract.—"A two-gram sample is weighed into an alundum or paper extraction thimble of 20 c.c. capacity and the extraction carried out for 1 hour, using any standard apparatus of the Soxhlet type. The weight of the residue after evaporation of the acetone is taken as the acetone extract. The extract for a pure carbon black is usually zero."

The estimated distribution of carbon black per annum produced in the United States is :

	Lbs.
Rubber industry	20,000,000
Printer's ink	10,000,000
Export	8,000,000
Stove polish	4,000,000
Phonograph records	500,000
Other Uses.	1,000,000

Under other uses are paint, carbon paper, type ribbon, tarpaulins, carriage cloth, black leather, paper, bookbinder's board, shoe polish, electric composition insulators, celluloid, buttons, etc. Considerable quantities are shipped to England, France, Japan and China. During pre-war times one-third of the annual production was exported.

Generally speaking, it may be said that carbon black is preferable for black printing ink, stove polish and vulcanised rubber, lamp-black being the better pigment, according to G. L. Cabot, for colouring oilcloth, leather and rubber, other than vulcanised, and generally for paint, although carbon black is preferable for certain kinds of paint and varnish. For further information, the reader may be referred to a paper by Perrott and Thiessen.⁴⁵

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CHAPTER V

LAMPBLACK

Methods of Production—Properties, Uses and Analyses.

LAMPBLACK is the soot or impalpable powder obtained from the smoke arising during the incomplete combustion of various carbonaceous substances such as vegetable and animal oils, pinewood and resinous materials. Soot has from time immemorial been used in painting and colouring a variety of objects, and it was the basis of the earliest known inks. The Chinese were probably the first to make it on an extensive scale for the manufacture of Chinese inks as known to the ancients. The method of manufacture was very primitive—and still is in China—the pigment being made by igniting resinous material in a pot in a closed room and leaving the material to burn itself out through lack of proper air supply.

Neither the yield nor the quality of the black could be considered satisfactory when produced in this way, and ordinary soot from the chimney back, once in common use as a pigment, is now discarded as being too impure owing to the amount of gritty and empyreumatic matter it contains, together with other impurities, and by reason of inferior colouring power.

The German method at one time was to burn resinous woods in a closed furnace and collect on woollen cloths, exposed to the smoke emitted, the resulting black.

In modern methods of manufacture the starting point is the dead oil of coal-tar works, an oil containing a large amount of naphthalene, some phenol and various aromatic hydrocarbons, particularly suited to the manufacture of lampblack by reason of the large percentage of carbon contained therein. These compounds, burnt in an insufficient supply of air, yield from 15 to 35% of their weight in the form of lampblack by deposition in suitably arranged chambers.

According to Cabot,³⁵ the quality of the black is determined by the size and shape of the furnaces in which the oil is burned, by the heat to which it is subjected during the progress of the manufacturing operation, by the position in which the black is deposited, and by the care exercised in selection of the raw materials employed.

The oil is normally allowed to flow in a sluggish stream into an earthenware or iron pot or pan, in which burning occurs, and from which the smoke passes through flues into the chambers in which the black is deposited.

The best grades of black, generally speaking, are obtained in furnaces of moderate size so built that the black is practically

calcined at the time it is deposited and carries down with it but little empyreumatic matter. The products of combustion are usually carried through a series of chambers, in which are partition walls, and the gases charged with lampblack are thus compelled to follow a tortuous path. The baffling effect of the partitions not only facilitates the deposition of the black, but may increase the percentage of deposition, though, of course, the placing of partitions can be overdone, and then the speed at which the gaseous products are impelled through the chambers becomes too great, leading to loss of black.

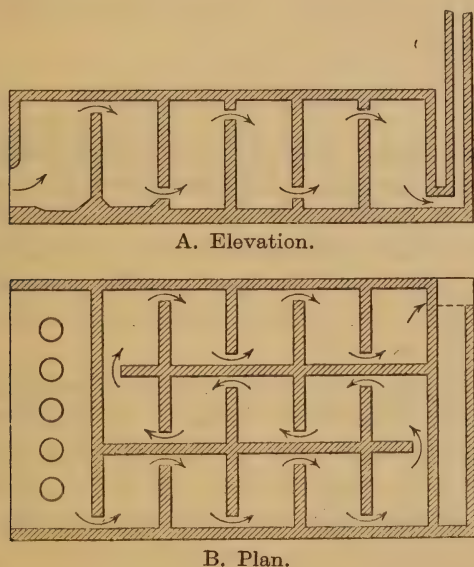


FIG. 12.—Arrangement of a Lampblack Plant.

The charging of lampblack furnaces must be performed quickly, to minimise the possibility of entry of large volumes of air into the furnaces and chambers owing to the risk of formation of explosive mixtures of air and the unconsumed combustible gases in the chambers or collectors, as they are also termed. The furnaces are kept at work for several days and then the chambers are allowed to cool gradually, care being necessary to admit the air only at a rate sufficient to remove any combustible gases from the chambers. Lampblack is very strongly pyrophoric, and therefore the greatest care is necessary in cooling it, for until it is cool it cannot be removed from the chambers.

The accompanying sketches (Fig. 12) indicate, in plan and elevation, the type of arrangement of a lampblack plant for securing

efficient deposition of the black. From time to time mechanical devices have been used in the form of stirrers to churn the air and cause the condensation of the smoke in masses sufficiently large for it to deposit itself.

Resin, resinous woods, tar and pitches are still to a small extent used in the manufacture of lampblack, though the product is said not to be so good as that from the dead oil of tar. The manufacture from hull bran has been described by Hershmann,⁴⁶ from peat by J. E. Smith,⁴⁷ and from coal-tar pitch by A. C. Evans and others.⁴⁸ By the incomplete combustion of oil,⁴⁹ the burning of oil fuel,⁵⁰ and in several other ways based on the use of coal tar,^{51, 52} lampblack may be obtained.

Properties of Lampblack.

Usually this contains about 80% of amorphous carbon, the rest being traces of resinous oils, empyreumatic matter, moisture, traces of adsorbed carbon dioxide and carbon monoxide and grit from the floors and walls of the collecting chambers. In contrast to carbon black, it has a grey hue. Its true specific gravity is 1.7 to 1.8 usually, and though it mixes well with oil and varnish, it does not generally mix with water.

The contrasting properties and qualities of lampblack and carbon black have been described by G. L. Cabot,^{19, 35} and from microscopic appearance it seems likely that in their structure these two black pigments differ from one another. As an explanation of this, Perrott² has put forward the suggestion that the difference may be due partly to the fact that as lampblack is made from a complex mixture of carbon compounds, each with its own optimum temperature of decomposition, a uniform product is less likely than might be expected in the case of carbon black produced from such a relatively simple raw material as natural gas.

The very best qualities of lampblack, known technically as vegetable black, are finer and softer in texture than ordinary lampblack, this vegetable black being the black deposited farthest away from the burning raw material. Such vegetable black is blacker than the commoner grade of lampblack, and is lower in ash and oily and empyreumatic matters. The term "vegetable black" is due to the circumstance that at one time the finer seed oils were used to produce this pigment. Tables X and XI (reprinted from Tables XIV and XV of *Bulletin*, 192) record the analyses of some lampblacks, particulars for other black pigments being given for contrast.

TABLE X.
Analyses of Carbon Blacks.

	Long black No. 1.	Long black No. 2.	Long black No. 3.	Short black No. 1.	Short black No. 2.	Short black No. 3.
PROXIMATE ANALYSIS.						
Moisture.....	3.56	7.13	5.30	2.25	3.02	3.12
Volatile matter.....	11.69	13.41	10.40	6.60	5.48	5.58
Fixed carbon.....	84.40	79.44	84.16	92.13	91.47	91.22
Ash.....	.05	.02	.14	.02	.03	.08
ULTIMATE ANALYSIS (AS RECEIVED).						
Hydrogen.....	1.10	1.32	1.11	.74	.88	1.05
Carbon.....	88.17	84.56	87.98	94.78	93.50	93.83
Nitrogen.....	.04	.04	.08	.09	.04	.05
Oxygen.....	10.54	14.00	10.88	4.37	5.25	5.19
Sulphur.....	.01	.06	.01	.00	.30	.00
Ash.....	.05	.02	.14	.02	.03	.08
ULTIMATE ANALYSIS (MOISTURE FREE).						
Hydrogen.....	.62	.57	.55	.50	.52	.72
Carbon.....	91.42	91.05	92.91	95.96	95.41	95.64
Nitrogen.....	.04	.04	.08	.09	.04	.05
Oxygen.....	7.66	8.28	6.30	2.43	2.69	2.51
Sulphur.....	.01	.06	.01	.00	.31	.00
Ash.....	.05	.02	.15	.02	.03	.08
True specific gravity.....	1.80	1.78	1.58	1.85	1.80	1.78

TABLE XI.
Analyses of Lampblacks and other Blacks.

	Lampblack.		Bone black.	Vine black.	Willow char- coat.	Wood pulp black.	Carbon from cracking of methane.	
	No. 1.	No. 2.					No. 1.	No. 2.
PROXIMATE ANALYSIS.								
Moisture.....	0.39	3.12	3.58	9.58	3.24	6.42	0.02	1.25
Volatile matter.....	2.26	17.38	10.92	29.54	14.66	9.78	.78	6.40
Fixed carbon.....	97.35	73.44	2.68	40.50	80.23	78.84	98.28	92.11
Ash.....	.00	.03	82.52	20.38	1.87	4.65	.84	.24
ULTIMATE ANALYSIS (AS RECEIVED).								
Hydrogen.....	.52	1.51	.88	2.44	2.74	1.60	.45	1.28
Carbon.....	97.62	87.84	8.64	51.65	85.04	83.20	98.70	95.76
Nitrogen.....	.11	.00	1.06	.80	.16	.17	.01	.01
Oxygen.....	1.18	9.95	6.84	24.41	10.11	9.59	1.61
Sulphur.....	.57	.84	.06	.32	.08	.48	.05	.12
Ash.....	.00	.06	82.52	20.38	1.87	4.96	.84	.24
ULTIMATE ANALYSIS (MOISTURE FREE).								
Hydrogen.....	.48	1.20	.47	1.53	2.46	.95	.45	1.13
Carbon.....	98.00	90.67	8.99	57.12	87.89	88.91	98.72	97.99
Nitrogen.....	.11	.00	1.10	.88	.17	.18	.01	.01
Oxygen.....	.84	7.41	3.53	17.58	7.47	4.1551
Sulphur.....	.57	.68	.06	.35	.08	.51	.05	.12
Ash.....	.00	.03	85.85	22.54	1.93	5.30	.02	.24
Acetone extract.....	.165	6.5002	.16

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CHAPTER VI

BLACK PIGMENTS IN PAINT MANUFACTURE

Consideration of the Physical Properties Involved—Various Uses of Black Pigment Paints—British Standard Specification for Carbon Black.

BLACK pigments find extensive use in various branches of the paint industry, and reference has already been made in earlier chapters to the use of metallic black pigments and particularly of graphite in this connection. The evaluation of black pigments according to their physical properties is of prime importance when considering the suitability of these pigments in the manufacture of paints, and the chief physical properties we must look at are as follows :—

1. Specific gravity.
2. Fineness.
3. Oil absorption.
4. Tinting strength.
5. Colour.

Chemical properties have been discussed in the earlier chapters and need not be touched upon again here. Such physical characteristics as covering power, hiding power, opacity, apply to pigments only when viewed in conjunction with paint media, and their study therefore does not really concern us here.

1. *Specific Gravity*.—The method of estimating this has been outlined in Chapter III, and for a pigment in a fine state of division is not quite as simple an operation as may be imagined. The sources of error lie in the difficulty of entirely removing entangled air and the difficulty of ensuring that the finest portions of the pigment are completely “wetted,” and it is therefore important that a proper vehicle should be selected in which to determine the specific gravity. In this connection the reader is referred to a paper by Nuttall ⁵³ on the “wetting power” of a liquid.

Increasing attention has been paid in recent years to the specific gravity of pigments, owing to the bearing this has on the volume of mixed paints, and also on the behaviour of pigments when suspended in liquid media. In some measure also there is a connection between the specific gravity of a pigment and the amount of oil required to grind the pigment into a uniform stiff paste, but this characteristic is more properly correlated with fineness.¹

Average Specific Gravity of Black Pigments with others for Comparison

Graphite	2.46	Red lead	8.80
Drop black	2.46	Zinc oxide	5.60
Bone black	2.35	White lead	6.60
Lamp black (vegetable		Barytes	4.45
black)	1.78	Ultramarine blue	2.50
Carbon black	1.80		

2. *Fineness*.—This as applied to pigments is usually understood to refer to the degree of subdivision of the particles, and has an important bearing on the paint industry. A certain degree of fineness is, of course, essential before the mixture of solid pigment with its liquid medium can be spread uniformly over a surface; moreover, the hiding power of a pigment is inversely proportional to the diameter of the particles, and furthermore the finer the particles of a given pigment when mixed to form a paint, the greater is its covering power.

The study of the ultimate size of particles, the determination of their size and the application of the results to the study of problems in the paint trade have engaged the attention of C. A. Klein and W. Hulme⁵⁴ and C. A. Klein and J. Parrish,^{55, 56} whose conclusions have appeared in recent publications. The chief methods which have been proposed for determination of particle size are :

(i) Screening followed by elutriation or sedimentation.

(ii) Direct examination under a microscope by a method due to Green.⁵⁷ A photomicrograph of a carefully prepared mounted sample is taken, and this is further enlarged by means of a stereopticon, the measurement being made of the particles on the screen by means of a millimetre scale. Green introduces a number of corrections in order to get a reliable value, but several objections have been made to some of his conclusions.

(iii) A centrifugal method due to Svedberg and Nichols.⁵⁸

(iv) Specific gravity suspension method due to Wiegner.⁵⁹

(v) Air flotation.

Space forbids any full treatment of the subject here, as we are concerned mainly with results obtained for black pigments and the bearing these results have on paint manufacture. According to the table by Klein and Parrish,⁵⁵ carbon black particles lie between 20 and 10μ ($1\mu = 10^{-6}$ metre), with a limiting size of 1μ . Now it is extremely unlikely that such a fine state of subdivision characterises those black pigments which after manufacture require mechanical grinding, such as the various charcoals, graphite, bone black, drop black; the bearing of this will be seen later.

Klein and Parrish⁵⁶ have pointed out the bearing of particle size, the effect of grinding and the influence of air-surround of pigments on the bulking value, which is of such importance in the paint industry. The figures given in Table XII, taken from their paper, are of interest, particularly the figures relating to oil absorption.

The authors discuss the various factors bearing on the bulking

value, and particularly mention the influence of the air-surround of the particles, which in the case of carbon black in the packed condition amounts to 80%.

TABLE XII.

Bulking Value and Oil Absorption of some Pigments.

Pigment.	Bulking value lbs./c. ft.		Air voids % for packed condition.	Oil absorption in gms. of oil per 100 gms. of pigment.
	Loose.	Packed.		
White lead A	44	125	71	12
Red lead B	103	233	58	8
Barytes	49	140	49	13
Carbon black	13	23	80	150
Ivory black	19	53	58	46

3. *Oil Absorption*.—At the present time consideration of the amount of oil or other medium required to convert a pigment into a paste ready for application in painting is an important matter, and is spoken of generally as the “oil absorption” of the pigment, though this term is capable of a varied interpretation, as Cruickshank Smith points out. The exact method of determination of this property leaves much to be desired. Calbeck⁶⁰ distinguishes between primary and secondary oil absorption of pigments, the former being the proportion of oil required to make a stiff paste, whilst the latter refers to the additional amount of oil necessary to produce a mixture of painting consistency. This author mentions the following factors as determining the oil absorption: (1) air voids to be filled, (2) wetting power of the oil, (3) nature of the surface of the solid particles, (4) specific surface or fineness of the pigment, (5) geometrical arrangement of the solid particles in the paste or paint.

Gardner¹² has given some figures showing the percentage of oil required for grinding pigments into average paste form, viz.: Carbon black 82%, lampblack, 72%, drop (bone) black, 60%, bone black 40%, graphite (pure), 40%, and for contrast one may cite white lead (sublimed), 10%, blanc fixé, 30%, barytes (natural), 9%, terra alba (gypsum), 22%.

4. *Tinting Strength*.—The tinting strength of a pigment is a most important desideratum to the paint manufacturer, and it is in virtue

of their tinctorial properties that pigments transmit their own specific hue or colour to other pigments or materials incorporated with them. The tinting strength as applied to blacks is the measure of their ability to impart a black hue to a definite weight of a standard white pigment. In testing any given black it is the rule to compare its tinctorial properties with a standard black pigment, and the following procedure is that proposed in connection with the use of American carbon black as a paint pigment.²

In making the test, weigh out accurately 0.100 gram of the black to be tested, and 10.0 grams of standard zinc white kept specifically for such a test as this. Transfer to a glass or marble slab, and add from a burette exactly 3.5 c.c. of refined linseed oil. Mix with a palette knife, and rub out thoroughly with the knife until no streakiness is observed when successive small portions are spread on a clear piece of window glass and viewed from the upper side. Ten minutes is usually the time for this operation. Follow the same procedure with the standard black. Then spread a small amount of each mixing side by side on a clear glass, such as a microscope object glass. Examination of the samples from the other side of the glass, particularly at the line where they overlap, will show a difference of tinting strength should any exist.

To make a quantitative estimation of the tinting strength of the sample as compared with the standard, more white is added to the stronger mixing until the colours match. A new sample of the stronger black is then weighed out, using the calculated amount of zinc white, and the process is repeated until mixes of the same colour are obtained. If, for example, it was necessary to mix 15 grams of zinc white with 0.1 gram of the standard to match a mixture of 10 grams of zinc white and 0.1 gram of the sample, the sample has $66\frac{2}{3}\%$ the strength of the standard.

5. *Colour*.—By the term colour is meant the relative blackness of the material when mixed with oil. In making the colour test, 0.3 gram of each of the blacks to be compared is added to each of a like number of portions of 1.3 c.c. of refined linseed oil from a burette. Mix thoroughly by means of a palette knife, spread side by side on a slip of glass, and compare the relative colour by viewing from the upper side of the glass.

The measurement of the colour of a pigment in terms of some agreed standards is possible by such means as the use of the Tintometer (Lovibond), the Colourmeter and other means, to which considerable attention has been paid in recent years. The reader is referred to the more recent volumes on colour manufacture and

colour testing for a fuller insight into the details of colour measurement (cf. Klein and Aston's volumes).

In considering the uses of the black pigments in paint-making, the purpose for which the paint is intended is of importance, and Cruickshank Smith mentions the following uses to which such a paint may be applied :

(a) Decorative work requiring a jet-black used chiefly as a self-colour ;

(b) Tinting or staining, requiring a finely-ground and very strong paint suitable for making grey or slate-coloured tones ;

(c) Protection of wood, iron or stone, or as an important ingredient in paints to be used in protecting one or other of these surfaces.

For decorative work alone, bone black is strongly favoured, carbon black being added sometimes to secure depth of colour. Often, however, such pigments are adulterated with barytes and whiting for cheapness.

Black paints for tinting and staining purposes must generally be lampblack or carbon black, and in conjunction with a white base the former gives a bluish-grey tone and the latter a brownish-grey tone. Blacks vary in colour and in their tinting strength—the less volatile matter a black contains the blacker its colour. But the tinting strength of blacks high in volatile matter is usually higher than that of blacks containing more free carbon. This fact may be due to the way in which the volatile matter is dispersed through the black ; this point will be discussed more fully in the next chapter in connection with the use of blacks as ink pigments.

Carbon black and lampblack absorb far more oil in grinding than is the case with mineral and bone blacks ; this is partly on account of their finer state of subdivision, but against this must be set the fact that paints from the former pigments have, in consequence of this finer state of subdivision, greater hiding power. Generally also the former blacks are unsurpassed for use in making certain black varnishes on account of their superior tinting strength ; carbon black has three times the tinting strength of some of the charcoal blacks, such as one from ground coconut charcoal.

As protective coverings, black paints are not used for general purposes, except in the case of graphite, which has been mentioned in this connection in Chapter II. In the preparation of black distempers for stone and wood, however, and in the manufacture of stove polishes, both carbon black and lampblack find great use.

The so-called grinding in oil of the blacks, or, more properly speaking, their incorporation in the oil or paint medium, can be carried out in the ordinary granite triple-roller paint mill in the case of paints which contain the relatively coarser mineral, bone or charcoal blacks. Where very fine lampblack or carbon black is concerned, the ordinary granite triple-roller mill is useless. Rollers with a very smooth face are used, and these are usually enclosed under a hood or cover, so that loss of pigment, owing to its extreme fineness, is prevented. The author has experienced cases where such covering was necessary even in the use of very finely-ground vegetable charcoal.

The following tests have been suggested ² in connection with the use of carbon black as a paint pigment :

Carbon Black for Paint Manufacture.

<i>Chemical tests.</i>	<i>Physical tests.</i>
Moisture less than 5% Ash less than 1.25%	Tinting strength not less than 95% of the strength of standard.

In connection with the use of carbon black as a pigment in aircraft manufacture, the following specification is extracted, by the kind permission of the British Engineering Standards Association, from their Report No. D. 30, November, 1921, official copies of which can be obtained from the Secretary of the Association, 28 Victoria Street, Westminster, S.W.1, price 2d., post free.

BRITISH ENGINEERING STANDARDS ASSOCIATION

British Standard Specification for Aircraft Material.

CARBON BLACK

1. *Description*.—The material shall consist of gas carbon black, containing not less than 96% of carbon.

2. *State of Division*.—The material shall be in a fine state of division, uniform in character and free from gritty particles. Five parts of the pigment shall grind to a stiff paste with 4 parts of castor oil (British Standard Specification 2 D. 5).

3. *Moisture, etc.*—The loss in weight on heating in an oven at 100° C. (212° F.) for 1 hour shall not exceed 3%.

4. *Matter Soluble in Water*.—The material shall contain not more than 0.1% of matter soluble in water and the aqueous extract shall show no acid reaction to methyl orange.

The test shall be carried out as described in Appendix I.

5. *Ether Extract*.—The material shall contain not more than 0.5%

of matter soluble in methylated ether (sp. gr. 0.720). This shall be determined by extraction in a Soxhlet apparatus for 2 hours.

6. *Ash*.—The amount of ash left on ignition shall not exceed 0.2%.

7. *Colour*.—The colour of the material shall closely match that of the Standard,* when determined by the method given in Appendix II.

NOTE.—By “match” in the above clause, shall be understood approximately matching when compared with the Standard in diffused daylight.

8. *Tinting Strength*.—The tinting strength of the pigment shall be not inferior to that of the Standard,* when determined by the method described in Appendix III.

APPENDIX I.

Method for the Estimation of Matter Soluble in Water.

Two grams of the material shall be moistened with alcohol and then boiled for 5 minutes with 200 c.c. of neutral distilled water and filtered. The reaction of the filtrate shall be determined towards methyl orange. An aliquot part of the filtrate shall then be evaporated to dryness and the residue weighed.

APPENDIX II.

Method for the Determination of Colour.

Four parts of the pigment shall be ground to a paste with 3 parts of castor oil (British Standard Specification 2 D. 5). 3.5 grams shall then be thinned with 50 c.c. of the following nitro-cellulose medium, and the resulting product brushed on doped Linen Aeroplane Fabric (British Standard Specification 3 F. 1).

Nitro-cellulose syrup, British Standard Specification	2 D. 8.	23.2 grams
Butyl acetate	2 D. 4.	15 c.c.
Alcohol	2 D. 9.	15 c.c.
Benzol	2 D. 10.	15 c.c.
Acetone	2 D. 22.	20 c.c.

APPENDIX III.

Method for the Determination of Tinting Strength.

One part of the pigment shall be mixed with 80 parts of zinc oxide (British Standard Specification D. 27) and ground to a paste with 50 parts of castor oil (British Standard Specification 2 D. 5).

This Specification was adopted by the Sectional Aircraft Committee on the 21st October, 1921, and approved on behalf of the Main Committee on the 5th November, 1921.

* The Standard consists of a piece of doped and varnished fabric prepared as described in Appendix II, which can be obtained on application to the Superintendent, Royal Aircraft Establishment, Farnborough.

When considering artists' pigments, the qualities most desirable are permanence, brilliance, purity of tone; and permanence is, of course, often a matter of conditions. In manufacturing the artists' black pigments the most frequently used blacks are carbon black, lampblack and bone black.⁶¹

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CHAPTER VII

BLACK PIGMENTS FOR INK MANUFACTURE

Different Classes of Work requiring Printing Ink—Properties of Blacks—Long and Short Blacks—Chemical, Physical and Practical Tests on Printing Ink Blacks—Some Photomicrographs of Ink Pigments.

It seems probable that the very earliest known inks had lampblack or some similar form of carbon as their base; all the ancient Egyptian inks appear to have been essentially carbonaceous in character. A. Lucas ⁶² has examined the remains of ink of the sixteenth century B.C., and shown it to be of carbon basis. According to Chinese historians, Chinese, or Indian ink as we term it, was made as far back as between 2697 B.C. and 2597 B.C. Vitruvius,⁶³ the Roman engineer (30 B.C.—A.D. 14), describes the preparation of an ink for decorative purposes, the soot from pitch-pine being the basis. Gradually, however, the transition from carbon inks to those made from gall nuts and iron salts took place in Europe, and this transition was probably complete by the Middle Ages so far as inks for writing purposes are concerned. For a full account, however, of the development of the ink-making industry from the earliest times to the present day the reader must turn to Mitchell and Hepworth.⁶⁴

With the invention of the printing press and its introduction into England by Caxton, lampblack as a pigment for printing ink came into universal use, and was used exclusively for this purpose until the advent of carbon black about 1864, since which date the latter pigment has been used to an increasing extent, and is now the principal pigment for black printing ink, which is, of course, the most important ink used in printing, the ink being composed of the black pigment in a vehicle such as boiled linseed oil, other oils used according to requirements being perilla, tung and some mineral oils. The main desiderata are thus the pigment and the oil or varnish in which it is mixed.

Printing inks are used in three main classes of work, viz. :

1. Those for ordinary typographic work,
2. Those for lithographic printing,
3. Those for depressed surface printing, *e.g.*, in copper-plate engraving work.

The modern rotary printing-presses require an ink that will dry sufficiently rapidly to enable the presses to be operated at a high speed, that will flow freely, possess great covering power and make instantaneous and legible impressions.²⁰ One lb. of carbon black mixed with 8 lbs. of oil and other materials will give sufficient ink

to print 2,250 copies of a 16-page newspaper of ordinary size or 90 copies of a 300-page octavo book.

Certain carbon blacks give a "short" ink, *i.e.*, an ink of buttery consistency which does not flow rapidly, and such an ink is eminently suitable in lithographic and offset work, in slow-speed presses, and for most half-tones. Lampblack does not give the best consistency, and is too grey in colour. On the other hand, there are carbon blacks especially desirable where fast-running presses are in use, such blacks yielding a fluid "long" ink, which has opacity enough to give a black letter. According to Underwood and Sullivan,⁶⁵ if a pigment mixed with a large quantity of oil remains stiff or cannot be drawn out into a string between the fingers, such pigment is said to be "short," and generally it happens that pigments showing this property are not suited to ink manufacture. On the other hand, an ink with a good flow and the property of being drawn out into a thread between the fingers is said to possess length, and the black which imparts these characteristics is said to be a "long" black.

The properties of the various black pigments and their value as ink-making pigments have been ably summarised by Underwood and Sullivan⁶⁵ and are given in tabular form thus :

TABLE XIII.
Properties of Blacks.

Name.	Top hue.	Under hue.	Oil absorption.	Fineness.
Bone black	Greenish-black	Brownish-black	Fairly low	Should be fairly fine, <i>i.e.</i> , there should still be some grain
Vine black	Greenish-black darker than bone black	Brownish-black	Fairly low	—
Carbon black ...	Deep black	Brownish-black	High	—
Lampblack	Deep black	Brownish-black	High	—
Mineral black ...	Brownish-black	Decided brown	Fairly low	Should be an impalpable powder
Magnetic pigment	Brownish-black	Decided brown	Low	
Manganese black	Brownish-black	Decided brown	Low	

Name.	Flow.	Shortness.	Fastness to light.	Atmospheric influences.
Bone black	Flows fairly well	Fairly short	No effect	No effect
Vine black	Flows fairly well	Fairly long	"	"
Carbon black ...	Poor	Short	"	"
Lampblack	Poor	Short	"	"
Mineral black ...	Good	Fairly long	"	"
Magnetic pigment	Good	Long	"	"
Manganese black	Good	Long	"	"

TABLE XIII (continued).

Name.	Drying.	Smoothness.	Abrasive qualities.	Incompatibility.
Bone black	Exerts no drying action	Does not make a smooth ink	Quite abrasive	Mixes with everything
Vine black	"	Does not make a smooth ink	Quite abrasive	"
Carbon black ...	"	Works up very smooth	Not abrasive	"
Lampblack	"	Works up smooth	Not abrasive	"
Mineral black ...	"	Does not make a smooth ink	Quite abrasive	"
Magnetic pigment	"	Works up very smooth	Not abrasive	"
Manganese black	"	Works up very smooth	Not abrasive	"

Name.	Value as an Ink-making Pigment.
Bone black	Of great value as a plate-printing ink material, although it must be mixed with vine black for colour and to give the proper working qualities.
Vine black	Of great value as a toner to mix with bone black to give colour and working qualities to black plate-printing inks.
Carbon black	The most important typographical black; in fact it is the base of all black typographical inks at the present day.
Lampblack	Not much used at present, as its place has been taken by the cheaper but similar carbon black.
Mineral black	} Used principally to mix with other blacks.
Magnetic pigment	
Manganese black .	

Such physical qualities and the methods of evaluating them as specific gravity, fineness, oil absorption, tinting strength and colour have already been discussed in the preceding chapter, and need not be dealt with again here, though in one way or another all have an interest to the ink-maker.

Chemical tests have been dealt with in Chapter IV, and in connection with the amounts of volatile matter in blacks it may be mentioned that the halo sometimes to be observed round letters in some old books and papers has been attributed by Irvine ²⁹ to the presence of tarry compounds such as chrysene, $C_{18}H_{12}$ (m. p. $250^{\circ}C.$), and pyrene, $C_{16}H_{10}$ (m. p. $148^{\circ}C.$), in the black used. Whilst there are no definite specifications laid down to which carbon blacks for ink-making must conform, the following have been suggested and are here re-printed from the *Bulletin* ²:

Printing Ink.

Chemical tests.

Moisture	less than 5.0%
Ash	less than 0.1%
Acetone extract .	less than 0.1%

Physical tests.

Colour	must match standard.
Tinting strength .	must equal standard.
Grit	none.

Practical Tests.—The black when made into ink must have satisfactory working qualities as determined by an actual run on the press for which the ink is intended. The ink must have satisfactory transfer, tack, drying properties, colour, and must print a sufficient number of pages per pound. The oil must not separate from the pigment and there must be no offset or smutting.

Testing Methods.—Chemical and physical tests are performed as previously described. Practical tests are to be made on the press for which the ink is intended. Specifications for tests to be made for which half-tone black ink is used are as follows :

1. *Non-separation of Oil from Pigment.*—The oil or varnish should not separate from the pigment either on the face of the type or cuts or in the fountain, but should be short enough to break up readily in the distribution and not “string.”

2. *Transfer.*—In transferring from type or cuts to paper the ink should leave the face of the type or cuts reasonably clean.

3. *Hardness.*—Ink should dry hard on the paper in 8 hours to admit of easy handling without damage or injury to the work, and should not pull the coating or the face from the paper, nor the face from the roller.

4. *Drying.*—Ink should not dry on the forme, rollers or distribution, so that it may be easily removed therefrom.

5. *Offset or Smutting.*—The ink must be able to carry sufficient colour to print clean and sharp, without offset or smut on sheets falling on top from the pressfly or in piling the work.

6. *Colour.*—The ink must dry a deep, solid carbon (not aniline) black, and not turn grey, nor have a metallic sheen or lustre, nor blister the face of the paper.

7. *Quantity Required.*—The weight of the amount used must be noted and averaged on a basis of 5,000 printed pages.

Methods to be used in making the Practical Tests.²

1. The practical test of half-tone black ink shall be made on the flat-bed presses in use in the Government Printing Office.

2. The test shall be made on coated book paper of the size, weight and quality in general use in the Government Printing Office.

3. The type or cut forme shall be previously “made ready” and the press otherwise in good condition to make a satisfactory run.

4. The forme, rollers, distribution, and ink fountain shall then be thoroughly washed and cleaned. The ink to be tested shall be



FIG. 13.—Photomicrograph showing Agglomerated Particles of Short Carbon Black, 2 hrs. after preparation on the Slide. Magnified 500 diameters.

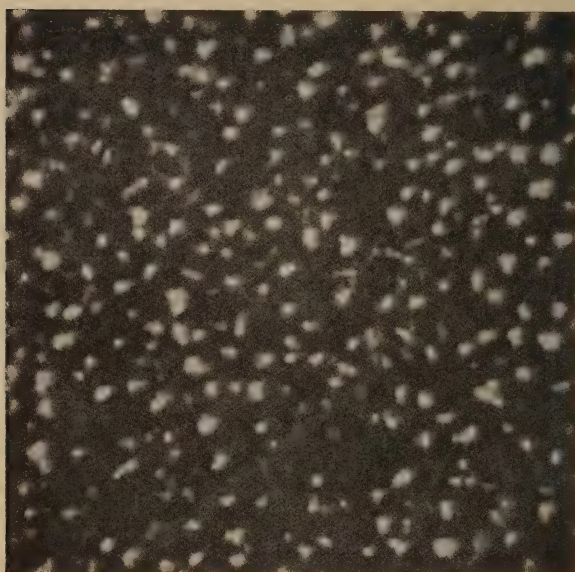


FIG. 14.—Photomicrograph showing Dispersed Particles of Long Carbon Black, 2 hrs. after preparation on the Slide. Magnified 500 diameters.

weighed before being placed in the fountain. The quantity to be tested should be sufficient to run not less than 3 hours, and preferably a run of 5 hours should be made.

5. Ink that will separate the oil or varnish from the pigment on the face of the forme or in the fountain will not be accepted.

6. To be satisfactory, ink, under the impression, should transfer from the face of the type or cuts to the paper, leaving the face of the type or cuts reasonably clean. It should be heavy in body, should feed well, and have sufficient "tack" to dry on the paper rapidly enough, while printing, to avoid the necessity of using slip sheets; but it should dry hard on the paper in 8 hours, so that the work can be handled easily without damage or injury to the printing. It must not pull the face or coating from the paper and leave it on the forme or pull the face from the rollers. It should be removed easily from the forme, rollers and distribution, and must be able to carry sufficient colour without offset or smut, and print clean and sharp.

7. The ink, to be satisfactory, must dry a deep, solid carbon (not aniline) black, and not turn grey, nor have a metallic sheen or lustre, nor blister the face of the paper.

Photomicrographs of carbon black have been taken by Dr. Reinhardt Thiessen and are reproduced here by the courtesy of the U.S. Department of the Interior from *Bulletin* 192. Under the microscope, freshly-prepared mixtures of thin lithographic varnish with short and long black respectively at first appear precisely similar. They consist of ultra particles or of agglomerates of two or three particles, but after a few minutes there is a progressive agglomeration of the particles to be noticed in the case of a "short" black and in about an hour there are groups with upwards of a hundred particles grouped together. In contrast, the "long" black remains completely dispersed even after an interval of several hours. These differences are admirably illustrated in Figs. 13 and 14.

Long blacks are usually made with cylindrical burners and a cool flame, a method tending to the production of a black high in volatile matter, and it is suggested that these impurities prevent carbon particles from agglomerating. The tendency towards agglomeration is materially altered by the character of the vehicle in which the blacks are suspended. Lampblack shows the same tendency to agglomerate as do short carbon blacks, and this fact is borne out by the appearance in Fig. 15. As a rule, however,

lampblacks make long inks, so that the tendency to agglomerate does not account entirely for the difference in behaviour of different carbon blacks and of lampblack.

Under the microscope lampblack and different grades of carbon black present much the same appearance. There are differences in the amounts of coarse particles, but the different behaviour of the various blacks may be due to a difference in the constitution of the ultramicroscopic particles, possibly a difference in size, in attraction between the particles, and in surface energy at the oil-black interface, but the reliable data available hardly warrant the putting forward of even a tentative explanation of the different behaviour of "long" and "short" blacks.

Preliminary study of (1) viscosity, (2) cohesion, and (3) adhesion of mixtures of black pigment and oil has been entered upon, and in some measurements which have been made long blacks are shown to have lower cohesion than short blacks, which is what one would expect from their behaviour. It seems reasonable to surmise that the physical considerations will outweigh the purely chemical in any hypothesis which satisfactorily explains the behaviour of different blacks, not only as ink pigments, but as paint pigments too.

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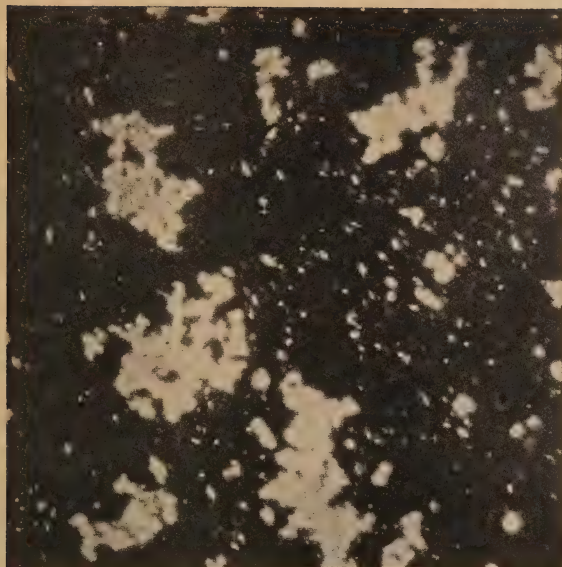


FIG. 15.—Photomicrograph showing Agglomerated Particles of Lampblack. Magnified 500 diameters.

CHAPTER VIII

CARBON BLACK AS A RUBBER PIGMENT

Factors concerned in the Use of Compounding Ingredients in Rubber—
Tests for Carbon Black in Rubber—Change in Elastic Constants—
Stress-strain Relationships.

PRIOR to the year 1914 carbon black and lampblack were used in the rubber industry only for colouring purposes, and to only a small extent. The presence of mineral ingredients in a fine state of subdivision in vulcanised rubber has long been recognised as capable of imparting desirable characteristics to such rubber, and a knowledge of the relative effects produced by different ingredients that may be used is of great importance.⁶⁶

Zinc oxide, which had early attained a position as an important filler for rubber, became too costly soon after the outbreak of the World War, and it was then shown that carbon black could be successfully substituted as a filler in rubber. The favourable results achieved increased the use of carbon black enormously, and the present tendency is to manufacture black tread tyres instead of white ones.²⁰ Since 1922 the demand from the rubber industry for carbon black has been so heavy that there has been a consequential expansion in the production of carbon black from natural gas in the United States, the production in 1923 being an increase of 104% over the production in 1922.⁶⁷

Carbon black as a rubber pigment is now used to the extent of 3—20%, according to the purpose for which the rubber is required. On a volume basis, carbon black (sp. gr. 1.8) costs only one-third of the price of zinc oxide (sp. gr. 5.6, say), but actually in practice a greater volume of carbon black is used than of zinc oxide, so that the resulting mix with the black contains less rubber per unit volume than the zinc oxide mix.

According to Greider,⁶⁸ the principal factors governing the reinforcing effects of all compounding ingredients in rubber appear to be :

1. Quantity of pigment or volume ratio pigment to rubber phase.
2. Average particle size (specific surface).
3. Wetting of pigment by rubber, or adhesion, surface tension.
4. Flocculation of the pigment during incorporation or vulcanisation.
5. Particle shape.
6. Uniformity or size-frequency distribution.

The influence of particle size on specific surface is of great importance in the rubber industry, and Wiegand,⁶⁹ in discussing the effect of surface area on the rubber stress-strain curve, gives the following figures :

Apparent Surface.

Barytes . . . 30,480 sq. ins. per c. in. of pigment.

Carbon Black . 1,905,000 „ „ „ „

The method of formation of carbon black is, of course, responsible for its fine state of subdivision and the corresponding enormous surface that ensues. Theoretically carbon black should be an ideal filler for rubber in virtue of its fine state of subdivision, because Ditmar⁷⁰ has found the following advantages accrue from the use of finely divided pigments in rubber mixtures :

1. The nearly homogeneous mixing.
2. The accelerated rate of cure.
3. The reduction in cost by the increase possible in the percentage of admixture.
4. Increase in elasticity.
5. The intensification of the colouring power.
6. The smoother surface obtained, and greater resistance to abrasion.
7. The longer life of the cured rubber.

Now in all the above respects carbon black has been found to be an ideal rubber pigment, and it is claimed for it, in addition, that it protects rubber from the action of light and, furthermore, may even retard oxidation.

The following tests have been suggested² for use in testing carbon black for the rubber industry :

TABLE XIV.

Carbon Black as a Filler for Rubber.

<i>Chemical tests.</i>	<i>Physical tests.</i>
Moisture less than 4%	Grit none (should completely pass through a 100-mesh sieve and feel as an impalpable powder when rubbed under the finger).
Acetone extract. less than 0.5%	
Ash less than 0.25%	Tinting
	strength . not less than 90% of the strength of standard.

Practical Tests.

Rubber mixes are made up containing equal weights of the sample to be tested and of the standard. Mixes are cured under exactly the same condition. The finished sheet is tested for tensile strength, per cent. elongation, toughness, and resistance to abrasion.

Wiegand ⁷¹ and Schippel ⁷² have investigated the volume increase of compounded rubber under strain, and also the stress-strain curves, and the results indicate generally that the finer the state of subdivision the larger the proportion of inert filler which can be mixed with rubber without resultant loss of tensile strength. In the case of carbon black, apparently up to 40% may be compounded, and the rubber is thus hardened and stiffened without loss of tensile strength. The volume increase at 200% elongation varies from 1.46% in the case of carbon black and 1.76% in the case of lamp-black to 13.3% in the case of barytes—zinc oxide apparently behaves somewhat abnormally.

TABLE XV.

The Results for Mixings containing 20 Volumes of Pigment

Pigment.	Apparent surface.	Displacement of stress-strain curve.	Total energy of resilience.	Volume increase % at 200% elongation.
Carbon black	1,905,000	42	640	1.46
Lampblack	1,524,000	41	480	1.76
Red oxide	152,400	29	355	1.9
Zinc oxide	152,400	25	530	0.8
Whiting	60,900	17	410	4.6
Fossil flour	50,800	14	365	3.5
Barytes	30,480	8	360	13.3

With the exception of zinc oxide, therefore, the increase in volume which occurs in compounded rubber when under strain is lowest when the particles are in the finest state of subdivision. The advantage of fine pigments relative to coarse ones is probably accounted for by the greater tendency of the compounded rubber, when stretched, to separate from the large particles.⁷³

The stress-strain curve for rubber reproduces in a simple manner the relation between the load and the elongation, and the displacement of the stress-strain curve refers to the increase in load supported at a given elongation, and is thus a measure of the resistance

to stretching. In respect of this property the behaviour of carbon black and lampblack is in accordance with the size of their particles.

W. W. Vogt and R. D. Evans ⁷⁴ have investigated the stress-strain relationship and Poisson's Ratio for all the common rubber compounding ingredients. For homogeneous isotropic substances the elastic constants and Poisson's Ratio are the same in all directions in the substance, but there are other substances where these constants and Poisson's Ratio have different values, and such latter substances are termed anisotropic.⁷⁵ As a result of their investigations, these authors find the following fillers are isotropic, viz.: carbon black, lampblack, zinc oxide, barytes, lithopone, whilst the following are anisotropic, viz.: graphite, mica, magnesium carbonate. It will be noted that graphite does not fall within the same category as carbon black and lampblack.

Similar differences were noted by the authors in regard to volume increase under strain and permanent set; the permanent set was higher for mixtures with anisotropic fillers than for those with isotropic ones, and mixtures containing anisotropic fillers on tearing behave as though laminated.

This anisotropy in properties is postulated as being due to the shape of the particles; particles with two dimensions notably greater than the third tend to align themselves during calendering with their longer axis in the direction of the calender, and their smaller dimension perpendicular to the plane of the calender. In consequence, different values for elastic constants and for Poisson's Ratio are obtained for a compounded rubber, according as to which of three mutually perpendicular directions is chosen to make the test, *i.e.*, with the grain, across the grain, or vertical to the grain.

The ultimate particles of lampblack and carbon black tend to approximate to the spherical shape from their very method of formation, and one would expect them therefore to be isotropic. The reader who is further inclined to pursue this study must consult some of the better-known works on rubber technology, to which domain the study properly belongs.

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⁷⁰ *Chem. Zeitung*, 1921, 45, 943. ⁷¹ *J. Ind. Eng. Chem.*, 1921, 13, 118. ⁷² *Ibid.*, 1920, 12, 33. ⁷³ *Annual Reports, Soc. Chem. Ind.*, 1919, 4, 324. ⁷⁴ Vogt and Evans, *J. Ind. Eng. Chem.*, 1923, 15, 1015. ⁷⁵ See Searle, "Experimental Elasticity," Camb. Univ. Press.

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CHAPTER IX

PITCHES AND BITUMINOUS MATERIALS

Introduction—Factors Involved in Classification—Definitions—Complete Classification.

Introduction and Classification

ON various parts of the earth's surface, notably in Syria, Egypt, Trinidad, Bermudez, California and Utah, occur mineral deposits, some of which are hard, brittle and black, whilst others are soft and viscous, black fluid masses. Allied to these in respect of many of their properties, and notably as regards applicability, are those black residues which arise out of the distillation, frequently destructive, of such familiar substances in the organic world as coal, wood, peat, petroleum, bone, fatty acids and greases. The terms Pitch, Asphalt, Asphaltum, Bitumen are variously and somewhat indiscriminately applied to these natural and manufactured products, and in consequence a certain confusion arises at times.

Many of these natural deposits have been known in the East from time immemorial, where their first use appears to have been in the nature of a cement for joining objects together. The word asphalt is traceable to Babylonian times, to the Greek *ἄσφαλτος*, through late Latin asphaltum to the French asphalté and ultimately the English asphalt. (Milton, *Paradise Lost*, i, 729, refers to "asphaltus"). The term bitumen originated in Sanskrit.

The earliest recorded use of asphalt by the human race goes back to the Sumerians, who were the pre-Babylonian ⁷⁶ inhabitants of the Euphrates valley. It was also known to the early Persians and to the ancient Egyptians, who used it in connection with their burial rites.⁷⁷ In the Old Testament there is reference to it in connection with the Tower of Babel (*circa* 2000 B.C.) and in connection with incidents relative to the infancy of Moses (*circa* 1500 B.C.).⁷⁸

From its earliest mention in the literature of Greece, Rome and Palestine, the typical asphalt of commerce was the solid bitumen, found on the shores of the Dead Sea, of the following proximate composition ⁷⁹:

Carbon	77.8%
Hydrogen	8.9%
Oxygen	11.6%
Nitrogen	1.7%

and closely analogous is the Egyptian bitumen :

Carbon	85.3%
Hydrogen	8.2%
Oxygen	6.25%
Nitrogen	0.25%

According to Nebuchadnezzar, his father Nabopolassar (625—604 B.C.) laid the first asphalt block pavement of which any record is extant.⁸⁰ Hannibal of Carthage (250 B.C.) used asphalt in warfare, and Pliny the Elder of Rome about A.D. 100 makes reference to asphalt, which, he says, must be glossy and black.

Asphalt was discovered in Cuba⁸⁰ in 1535, and the Pitch Lake in Trinidad⁸⁰ by Sir Walter Raleigh in 1595. In 1661 we find reference to the production of wood tar on the large scale by the dry distillation of wood, and later, in 1681, the discovery of coal tar pitch was made in England, a patent relative thereto being taken out by Becher and Serle.⁸⁰

During the nineteenth century many advances were chronicled in connection with our knowledge of asphaltic and pitch-like substances, and the first use of the asphalt pavement is to be recorded in London, Paris and the large cities of U.S.A. Such natural bitumens as gilsonite were discovered in Utah in 1885, and the same century saw the manufacture and use of stearine pitch and petroleum pitch—residues of the distillation of fatty acids and petroleum respectively.

As already mentioned, owing to the loose and indiscriminate way in which the terms “bitumen,” “tar,” “pitch,” “asphalt,” etc., have been used for centuries, coupled with the fact that the physical properties and the chemical composition of the substances so designated were little understood, the problem of accurately defining and systematically classifying the various pitches and bituminous substances has proved extraordinarily baffling. At the present time there is no uniform or accepted standard of nomenclature, though much has been done towards evolving order out of chaos by the work of Abraham,⁸¹ Clifford Richardson⁸² and the British Engineering Standards Association.⁸³ In his recently published book, P. E. Spielmann^{83a} has reviewed at some length and somewhat chronologically the various attempts that have been made to secure uniformity of definition and nomenclature of Bituminous Substances. The present author⁸⁴ in an earlier publication used the term bitumen to define a class of substances, not necessarily solid, occurring in nature, and which are soluble in carbon disulphide, chloroform and other neutral liquids, and consisting essentially of compounds of carbon and hydrogen asso-

ciated frequently with compounds of oxygen, sulphur and nitrogen with possibly traces of mineral matter, the latter consisting of compounds of iron and alumina. Adopting this definition, one would then regard the asphalts as mineral matters containing bitumen in intimate association. Richardson has suggested the term "residual pitches" for those closely allied artificial products arising during the distillation of organic bodies.

Broadly speaking, the foregoing is in substantial agreement as regards its main outlines with the more elaborate and detailed system of definition and classification adopted by Abraham,⁸⁰ and the present author has adopted in this volume the system of Abraham, except in respect of certain substances which have been omitted from that writer's scheme for reasons which will be indicated later.

The following criteria, viz., origin, physical properties, solubility and chemical composition, form the basis for a preliminary classification indicated in the accompanying table :

TABLE XVI ⁸⁰

Origin	Native	{ Mineral
		{ Vegetable
		{ Animal
	Pyrogenous	{ Evaporation (fractional distillation)
		{ Destructive distillation
		{ Heating in a closed vessel
		{ Blowing with air
Physical properties	Colour in mass	{ Light (white, yellow or brown)
		{ Dark (black)
	Consistency or hardness	{ Liquid
		{ Viscous
		{ Semi-solid
		{ Solid
	Fracture	{ Conchoidal
		{ Hackly
	Lustre	{ Waxy
		{ Resinous
		{ Dull
	Feel	{ Adherent
		{ Non-adherent
Solubility	Odour	{ Unctuous (waxy)
		{ Oily (petroleum-like)
	Tarry	{ Volatile
		{ Non-volatile
	Fusibility	{ Fusible
		{ Difficultly fusible
		{ Infusible (melts only with decomposition)
Chemical composition	Solubility	{ Non-mineral constituents in carbon disulphide
		{ Distillate at 300 to 350° C. in sulphuric acid (<i>i.e.</i> "sulphonation residue")
	Chemical composition	{ Hydrocarbons (compounds containing carbon and hydrogen)
		{ Oxygenated bodies (compounds containing carbon hydrogen and oxygen)
		{ Crystallisable paraffins (crystallise at low temperatures)
		{ Mineral matter (inorganic substances)

Bituminous substances.	Origin.	Physical properties.						Solubility.		Composition.
		Colour in mass.	Consistency.	Lustre.	Feel.	Odour.	Volatility.	Fusibility of non-mineral constituents.	Non-mineral constituents in carbon disulphide.	
Bitumen	Native	Variable (light to dark)	Variable (liquid to solid)	—	—	—	Variable	Harder varieties are fusible	Largely soluble	Considerable
Pyro-bitumen	Native	Dark	Comparatively hard	Resinous to dull	Non-adherent	—	Non-volatile	Infusible	Relatively insoluble	—
Asphalt	Native or pyrogenous	Dark	Variable	Harder varieties, resinous to dull	Adherent to non-adherent	—	Comparatively non-volatile	Fusible	Largely soluble	Considerable
Asphaltite	Native	Dark	Comparatively hard	Resinous	Non-adherent	—	Non-volatile	Difficultly fusible	Largely soluble	Considerable
Asphaltic pyro-bitumen	Native	Dark	Comparatively hard	Resinous to dull	Non-adherent	—	Non-volatile	Infusible	Largely insoluble	—
Non-asphaltic pyro-bitumen	Native	Dark	Comparatively hard	Resinous to dull	Non-adherent	—	Non-volatile	Infusible	Largely insoluble	—
Tar	Pyrogenous	Dark	Liquid	—	Oily	Characteristic ("Tarry")	Comparatively volatile	—	Largely soluble	Comparatively little
Pitch	Pyrogenous	Dark	Viscous to solid	Resinous to dull	Adherent to non-adherent	—	Comparatively non-volatile	Fusible	Largely soluble	Comparatively little

In Table XVII the most important types of bituminous substances and pitches are classified according to the features enumerated in Table XVI. Abraham, in his system of classification, has included the Mineral Waxes amongst the bituminous substances, but since these waxes, such as ozokerite and montan wax, are so closely akin to paraffin wax, at any rate in general physical properties and to a considerable extent in chemical composition, it appears preferable to exclude these waxes from the scheme of classification. Furthermore, the present author does not deem it advisable to include, as Abraham does, Petroleum. It appears better to consider petroleum as the parent substance of certain bitumens rather than as a species of bitumen itself, and there is ample evidence to support this preference, and consequently petroleum is not included in Table XVIII.

The definitions which follow are taken from Abraham's classification,⁸⁰ and they help to a clear understanding of Table XVII and to that of Table XVIII, which follows in further elaboration.

Bitumen.—A term applied to native substances of variable colour, hardness and volatility; composed of hydrocarbons and substantially free from oxygenated bodies; sometimes in association with mineral matter, the non-mineral constituents being fusible and largely soluble in carbon disulphide; and whose distillate, fractionated between 300° and 350° C., yields considerable sulphonation residue.

This definition includes petroleum and native mineral waxes, which the author, however, prefers not to include in any system of classification of bitumens.

Pyrobitumen.—A term applied to native substances of dark colour, the word "pyrobitumen" implying that the substances, when subjected to heat, will give rise to bodies resembling bitumens in their solubility and physical properties. They are comparatively hard and non-volatile; composed of hydrocarbons, which may or may not contain oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being infusible and relatively insoluble in carbon disulphide.

Asphalt.—A term applied to a species of bitumen and also to certain pyrogenous substances of dark colour, of variable hardness, comparatively non-volatile; composed of hydrocarbons, substantially free from oxygenated bodies; containing relatively little or no crystallisable paraffins; sometimes in association with mineral matter, the non-mineral constituents being fusible, and largely soluble in carbon disulphide; and whose distillate, fractionated

between 300° and 350° C., yields considerable sulphonation residue.

Asphaltite.—A species of bitumen, including dark-coloured, comparatively hard and non-volatile solids; composed of hydrocarbons, substantially free from oxygenated bodies and crystallisable paraffins; sometimes associated with mineral matter, the non-mineral constituents being difficultly fusible, and largely soluble in carbon disulphide, and whose distillate, fractionated between 300° and 350° C., yields considerable sulphonation residue.

Asphaltic Pyrobitumen.—A species of pyrobitumen including dark-coloured, comparatively hard and non-volatile solids; composed of hydrocarbons, substantially free from oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being infusible and largely insoluble in carbon disulphide.

Non-asphaltic Pyrobitumen.—A species of pyrobitumen, including dark-coloured, comparatively hard and non-volatile solids; composed of hydrocarbons, containing oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being infusible and largely insoluble in carbon disulphide.

Tar.—A term applied to pyrogenous distillates of dark colour, liquid consistency, having a characteristic odour; comparatively volatile; of variable composition; sometimes associated with carbonaceous matter, the non-carbonaceous constituents being largely soluble in carbon disulphide, and whose distillate, fractionated between 300° and 350° C., yields comparatively little sulphonation residue.

Pitch.—A term applied to pyrogenous residues, of dark colour, viscous to solid consistency; comparatively non-volatile, fusible; of variable composition; sometimes associated with carbonaceous matter, the non-carbonaceous constituents being largely soluble in carbon disulphide, and whose distillate, fractionated between 300° and 350° C., yields comparatively little sulphonation residue.

The preceding definitions allow construction of the detailed classification in Table XVIII. This latter agrees with that of Abraham, except that petroleum and native mineral waxes have not been included, whilst the non-asphaltic members (peat, lignite, coal and their shales) have been omitted, as likewise also have the pyrogenous waxes, though included by Abraham. The present author considers all such substances quite outside such a classification.

TABLE XVIII
COMPLETE CLASSIFICATION OF BITUMINOUS SUBSTANCES⁸⁰

Genus.	Species.	Member.	Remarks.
Bitumens	Native asphalts	Pure or fairly pure Associated with mineral matter	Comparatively free from associated mineral matter (less than 10% on the dry weight). Containing a substantial portion of sand, sandstone, limestone, clay or shale.
	Asphaltites	Gilsonite Glance pitch Grahamite	Extremely pure Pure to moderately pure } Have a higher fusing-point than asphalts. Pure to quite impure } Derived from petroleum.
	Asphaltic pyrobitumens	Elaterite Wurtzilite Albertite Impsonite Asphaltic pyrobituminous shales	Rubbery—partly saponifiable Depolymerises on heating, becoming fusible and soluble } Generally pure. Infusible and insoluble. Derived from petroleum. Depolymerises partly on heating } Does not depolymerise on heating } Mineral matters predominate. Infusible and insoluble.
Pyrogenous distillates	Tars	Oil-gas tar Water-gas tar	Produced by cracking petroleum vapours in manufacturing oil-gas. Produced by cracking petroleum vapours in manufacturing carburetted water-gas.
		Pine-tar Hardwood tar Peat tar	Produced by the destructive distillation of the woods and roots of coniferae. Produced by the destructive distillation of hardwoods.
		Lignite (brown coal) tar Shale tar Gas-works coal-tar Coke-oven coal-tar	Produced by the destructive distillation of peat. Produced by the destructive distillation of lignite (brown coal). Produced by the destructive distillation of pyrobituminous shales. Produced from gas-house retorts in manufacturing gas from bituminous coal. Produced from by-product coke-oven in manufacturing coke from bituminous coal.

		<p>Blast-furnace coal-tar</p> <p>Producer-gas coal-tar</p> <p>Bone-tar</p>	<p>Produced from blast-furnaces upon smelting metals with bituminous coal.</p> <p>Produced from gas-producers in manufacturing producer-gas from coal.</p> <p>Produced by the destructive distillation of bones.</p>
		<p>Residual oils</p>	<p>Produced by the dry distillation of non-asphaltic petroleum, the dry or steam-distillation of mixed base petroleum, or the steam distillation of asphaltic petroleum.</p>
	Pyrogenous asphalts	<p>Brown petroleum asphalts</p> <p>Residual asphalts</p> <p>Sludge asphalts</p> <p>Wurtzilite asphalt</p>	<p>Produced by blowing air through heated residual oils.</p> <p>Produced by the steam distillation of mixed-base and asphaltic petroleum.</p> <p>Produced from the acid sludge, obtained in the purification of petroleum distillates with sulphuric acid.</p> <p>Produced by depolymerising wurtzilite in closed retorts.</p>
Pyrogenous residues.		<p>Oil-gas-tar pitch</p> <p>Water-gas-tar pitch</p> <p>Wood-tar pitch</p> <p>Peat-tar pitch</p> <p>Lignite-tar pitch</p> <p>Shale-tar pitch</p> <p>Gas-works coal-tar pitch</p> <p>Coke-oven coal-tar pitch</p> <p>Blast-furnace coal-tar pitch</p> <p>Producer-gas coal-tar pitch</p> <p>Bone-tar pitch</p> <p>Rosin pitch</p> <p>Fatty-acid pitch</p> <p>Cotton-seed pitch</p> <p>Wool pitch</p>	<p>Residues obtained by the partial evaporation or distillation of the respective tars.</p>
	Pitches		<p>Residue obtained by the partial distillation of the resinous sap of conifera.</p> <p>Residue obtained by the steam distillation of fatty acids.</p> <p>Residue obtained by the steam distillation of cotton black grease.</p> <p>Residue obtained by the steam distillation of brown wool grease</p>

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CHAPTER X

THE CHEMISTRY OF THE BITUMENS AND PITCHES

Paraffinoid, Aromatic and Naphthenic Hydrocarbons—Nitrogenous, Oxygenated and Sulphur Compounds.

THE bitumens and pyrobitumens occurring in nature as well as the somewhat related manufactured pitches are complex mixtures of chemical compounds containing the elements carbon and hydrogen—the Hydrocarbons—in varying proportions and combined in a variety of ways. Some of the compounds may contain the elements oxygen, sulphur and nitrogen, and smaller or larger amounts of extraneous mineral matter are usually found in intimate association. Hydrocarbons occur in all types of bituminous substances—in fact, they predominate—and they are briefly considered below :

Hydrocarbons.—The following series are known to occur :

C_nH_{2n+2} Series—Paraffins.

	Name.	Formula.	M. p. (° C.).	B. p. (° C.).
<i>Liquid :</i>	Pentane	C_5H_{12}	—	+38
	Hexane	C_6H_{14}	—	+69
	Heptane	C_7H_{16}	—	+98
	↓	↓		
<i>Solid :</i>	Heptadecane	$C_{17}H_{36}$	22	—
	Octodecane	$C_{18}H_{38}$	28	317
	Nonadecane	$C_{19}H_{40}$	32	330
	Eicosane	$C_{20}H_{42}$	37	205
	↓	↓		at 15 mm.
	Dimyricyl	$C_{60}H_{122}$	102	—

The liquid members and their isomers are associated together in such petroleum as that of Pennsylvania and in certain asphalts, whilst some of the solid members occur in low-temperature tars from coal.

C_nH_{2n} Series—Olefines (one double bond).

	Name.	Formula.	M. p. (° C.).	B. p. (° C.).
<i>Liquid :</i>	Amylene and isomers	C_5H_{10}	—	+39
	Hexylene "	C_6H_{12}	—	69
	Heptylene	C_7H_{14}	—	95
	↓	↓		
<i>Solid :</i>	Eikosylene	$C_{20}H_{40}$	—	314
	Cerotene	$C_{27}H_{54}$	+58	—
	Melene	$C_{30}H_{60}$	+62	375

These and their isomers are present in some American petroleum in small amount.

C_nH_{2n-2} Series—*Acetylenes* (one triple bond).

	Name.	Formula.	B. p. (° C.).
Liquid :	Crotonylene	C_4H_6	27
	Isopropylacetylene	C_5H_8	—

Several of the higher members are found in Texas, Louisiana and Ohio petroleum and in coal tar.

C_nH_{2n-2} Series—*Diolefines* (two double bonds).

	Name.	Formula.	B. p. (° C.).
	Allylene (Propadiene)	$CH_2:C:CH_2$	Gas
	Divinyl (Erythrene)	$CH_2:CH:CH:CH_2$	—5
	Piperylene (α -Methylbutadiene)	$CH_2:CH:CH:CH:CH_3$	+42
	Isoprene (β -Methylbutadiene)	$CH_2:CH:C(CH_3):CH_2$	+35
	↓	↓	
	Conylene	$CH_2:CH:CH_2CH:CH:CH_2CH_2CH_3$	126

These hydrocarbons occur in tars and in certain petroleum.

C_nH_{2n-4} Series—*Olefinacetylenes*.

Some of these occur in certain types of Californian petroleum.

C_nH_{2n} Series—*Naphthenes or Cycloparaffins or Polymethylenes*.

	Name.	Formula.	M. p. (° C.).	B. p. (° C.).
	Cyclopropane (Trimethylene)	$CH_2 \begin{matrix} \diagup CH_2 \\ \diagdown CH_2 \end{matrix}$	—126	—35
	↓			
	Cyclohexane (Hexamethylene)	$\begin{matrix} CH_2-CH_2-CH_2 \\ \\ CH_2-CH_2-CH_2 \end{matrix}$	+6	81
	↓			
	Cyclononane (Nonomethylene)	$\begin{matrix} CH_2-CH_2-CH_2-CH_2 \\ \\ CH_2-CH_2-CH_2-CH_2 \end{matrix} > CH_2$		171

These occur in American mixed-base and asphaltic petroleum (including Ohio, Californian and Canadian) and in fatty acid pitches.

C_nH_{2n-2} Series—*Polycyclic Polymethylenes*.



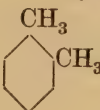
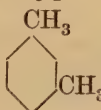
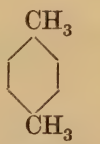
These are usually associated with members of the previous series.

C_nH_{2n-2} Series—Cyclo-olefines (one double bond).

These include cyclo-ethylene, C_4H_6 , $\begin{array}{c} CH=CH \\ | \quad | \\ CH_2-CH_2 \end{array}$, and cyclo-propylene, C_5H_8 , $\begin{array}{c} CH=CH \\ / \quad \backslash \\ CH_2-CH_2-CH_2 \end{array}$.

They occur in Texas oils and in certain asphalts.

C_nH_{2n-6} Series—Monocyclic Benzenes.


Name.	Formula.	B. p. (° C.).
Benzene	C_6H_6 or 	80
Toluene or Monomethylbenzene	$C_6H_5 \cdot CH_3$ or 	110
Xylenes	$C_6H_4(CH_3)_2$	
or Dimethylbenzenes	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  ortho- b. p. 142°. </div> <div style="text-align: center;">  meta- b. p. 139°. </div> <div style="text-align: center;">  para- b. p. 138°. </div> </div>	
Trimethylbenzenes (3)	$C_6H_3(CH_3)_3$	
↓	↓	
Hexamethylbenzene	$C_6(CH_3)_6$	305


Members of this series and their respective isomers are present in coal tars, water gas tar and other pyrogenous distillates. Traces have been found in many petroleum and in lignite tar.


C_nH_{2n-8} to C_nH_{2n-30} Series—Monocyclic and Polycyclic.

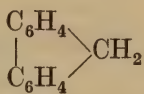

C_nH_{2n-8} Series, of which the principal member is phenylethylene, $C_6H_5 \cdot CH:CH_2$.


C_nH_{2n-10} Series—the *Indenes*, of which the principal members are indene, $C_6H_4 \cdot C_3H_6$, b. p. 182° C., hydrindene, $C_{10}H_{10}$, b. p. 176° C., and the methylindenes and dimethylindenes.


C_nH_{2n-12} Series—the *Naphthalenes*, the principal member of which is naphthalene, $C_{10}H_8$, represented thus : .


C_nH_{2n-14} Series—the *Diphenyls*, the principal member of which is diphenyl, $C_{12}H_{10}$, represented as . The next member of the series is methyl diphenyl, $C_{12}H_9 \cdot CH_3$.

C_nH_{2n-14} Series—the *Acenaphthenes*, the first member of which is acenaphthene, $C_{12}H_{10}$, which is represented as .

C_nH_{2n-16} Series—the *Diphenylenes*, which include fluorene, $C_{13}H_{10}$, represented as  or ; stilbene, $C_6H_5 \cdot CH:CH \cdot C_6H_5$.

C_nH_{2n-18} Series—the *Anthracenes*, of which the chief members are anthracene, $C_{14}H_{10}$, represented as , b. p. $351^\circ C$;

phenanthrene, $C_{14}H_{10}$, represented as , b. p. $340^\circ C$;

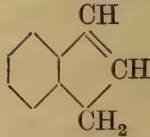
retene, $C_{18}H_{18}$, , b. p. $350^\circ C$.

C_nH_{2n-20} Series—principal member fluoranthene, $C_{15}H_{10}$.

C_nH_{2n-22} Series—principal member pyrene, $C_{16}H_{10}$.

C_nH_{2n-24} Series—principal member chrysene, $C_{18}H_{12}$.

The hydrocarbons of all the foregoing series, C_nH_{2n-8} to C_nH_{2n-30} , all occur in coal tar and the higher members of many

of the series in coal-tar pitch. Indene, , $C_6H_4 \cdot C_3H_4$,

and styrene, $C_6H_5 \cdot CH:CH_2$, have been identified, and their respective amounts present determined by R. L. Brown and R. D. Howard ⁸⁵ recently in samples of water-gas tar, whilst J. M. Weiss and C. R. Downs ⁸⁶ have isolated 4% of phenanthrene, $C_{14}H_{10}$, and 0.1% of diphenyl, $(C_6H_5)_2$, from coke-oven tar.

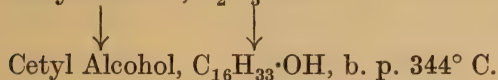
Oxygen-containing Compounds.

Water occurs in small quantities in most native asphalts, in crude tars and to some extent in pitches.

Alcohols :

Methyl Alcohol, $\text{CH}_3\cdot\text{OH}$.

Ethyl Alcohol, $C_2H_5 \cdot OH$.



Ceryl Alcohol, $C_{26}H_{53}\cdot OH$, m. p. $79^{\circ} C$.

Myricyl Alcohol, $C_{30}H_{61}\cdot OH$, m. p. $88^{\circ} C$.

The higher waxy members of this series are present in wool wax or grease and in wool grease pitch and in certain bitumens.

Ketones :

Acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$, and its higher homologues are found in wood tar and certain lignite and blast-furnace tars.

Phenols :

Phenol, C_6H_5OH , b. p. $182.6^\circ C$.

Cresol or Methyl Phenol (3 isomers), $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$.

Dihydric Phenols (3 isomers), $C_6H_4(OH)_2$.

Guaiacol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3$.

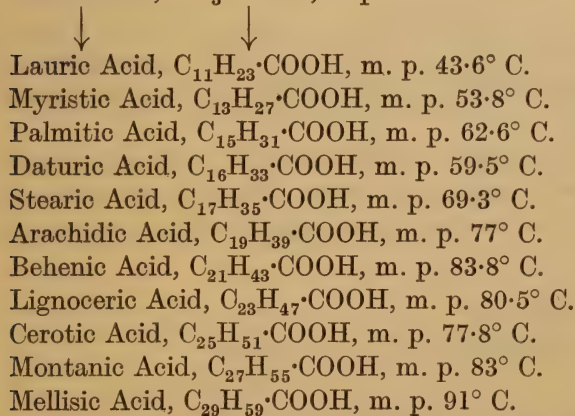
Trihydric Phenols, $C_6H_3(OH)_3$.

These and higher homologues and derived esters are found in coal tar and lignite tar, whilst guaiacol and other esters of the cresols and the trihydric phenols are found in wood tar and wood-tar pitch.

Fatty Acids :

$C_nH_{2n}O_2$ Series :

Acetic Acid, $\text{CH}_3\cdot\text{COOH}$, b. p 137.9°C .



Myristic Acid, $C_{13}H_{27}\cdot COOH$, m. p. $53.8^{\circ} C$.

Palmitic Acid, $C_{15}H_{31}\cdot COOH$, m. p. $62.6^{\circ} C$.

Daturic Acid, $C_{16}H_{33} \cdot COOH$, m. p. $59.5^{\circ} C$.

Stearic Acid, $C_{17}H_{35}\cdot COOH$, m. p. $69.3^{\circ}C$.

Arachidic Acid, $C_{19}H_{39}\cdot COOH$, m. p. $77^{\circ} C$.

Behenic Acid, $C_{21}H_{43}COOH$, m. p. $83.8^{\circ}C$.

Lignoceric Acid, $C_{23}H_{47}\cdot COOH$, m. p. $80.5^{\circ} C$.

Cerotic Acid, $C_{25}H_{51}\cdot COOH$, m. p. $77.8^{\circ}C$.

Montanic Acid, $C_{27}H_{55}\cdot COOH$, m. p. $83^{\circ} C$.

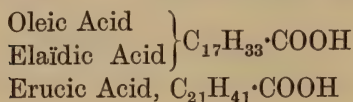
Mellistic Acid, $C_{29}H_{59}\cdot COOH$, m. p. $91^{\circ} C$.

Acetic acid is present in wood tars, whilst the higher members

of this series from palmitic acid upwards, together with their corresponding lactones and esters, are found in fatty acid pitches, and the members from cerotic acid upwards in wool grease pitch and in certain bitumens.

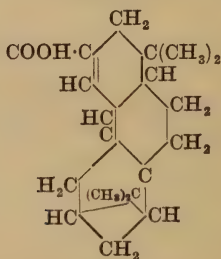
$C_nH_{2n-2}O_2$ Series :

Amongst the higher members are



Some of the higher members of this series are found in fatty acid pitches.

Resin Acids.—These are of somewhat uncertain structure, but the abietic acids and their homologues containing a phenanthrene or retene hydrocarbon structure are known to occur in rosin oil, and are probably present, together with their esters, anhydrides and lactones, in wood tars, especially pine tar, in pine pitch and in resin pitch. Various constitutions of the type represented by Grün, viz.,




$C_{20}H_{30}O_2$, have been attributed to abietic acid, but at present the constitution of this and of allied resin acids is undecided, though an able summary of our present knowledge has been contributed by C. E. Soane.⁸⁷


A number of highly complex resinous and oxygenated compounds are found in many of the soft naturally occurring asphalts, but their complete separation and identification have not yet been achieved.

Sulphur Compounds :

Carbon Disulphide, CS_2 , b. p. $46.5^\circ C$.

Thiophene, C_4H_4S , represented as , b. p. $84^\circ C$.

α -Thiotolene, $\text{CH}_3 \cdot \text{C}_4\text{H}_3 \cdot \text{S}$ or , b. p. 112°C .

β -Thiotolene, $\text{CH}_3 \cdot \text{C}_4\text{H}_3 \cdot \text{S}$ or , b. p. 113°C .

Thioxenes and their isomers, $\text{C}_4\text{H}_2\text{S}(\text{CH}_3)_2$.

Methyl Sulphide, $(\text{CH}_3)_2\text{S}$, b. p. 37.5°C .

Ethyl Sulphide, $(\text{C}_2\text{H}_5)_2\text{S}$, b. p. 92°C .


Methyl Mercaptan, $\text{CH}_3 \cdot \text{SH}$, b. p. 6°C .

Ethyl Mercaptan, $\text{C}_2\text{H}_5 \cdot \text{SH}$, b. p. 36.2°C .

Some or all of the above compounds are known to occur in certain petroleum, their derived asphalts, in certain pyrobitumens, notably in coal tar and lignite tar, and probably in the corresponding pitches.

Nitrogenous Compounds :


Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, b. p. 183°C .


Pyridene, $\text{C}_5\text{H}_5\text{N}$, represented as , b. p. 115°C .

Picolines or Methyl Pyridines (3 isomers), $\text{CH}_3 \cdot \text{C}_5\text{H}_4\text{N}$.


Lutidines or Dimethyl Pyridines (4 isomers), $(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}$.


Collidines or Trimethyl Pyridines, $(\text{CH}_3)_3\text{C}_5\text{H}_2\text{N}$.

Indol, $\text{C}_8\text{H}_7\text{N}$, represented as 

Quinoline, $\text{C}_9\text{H}_7\text{N}$, represented as 

Isoquinoline, $\text{C}_9\text{H}_7\text{N}$, represented as  and their homologues.

Acridine, $\text{C}_{13}\text{H}_9\text{N}$, represented as 

Pyrrol, $\text{C}_4\text{H}_5\text{N}$, represented as , b. p. $130-131^\circ \text{C}$.

Carbazol, $\text{C}_{12}\text{H}_9\text{N}$, b. p. 238°C .

Very small amounts of some of the foregoing are found in

fatty acid pitches, though all are present in coal tar; some are present in petroleum asphalts and lignite tar and the less volatile in coal-tar pitch and lignite-tar pitch.

It is evident that the chemistry of bituminous substances and pitches is very complicated in view of the fact that their composition is not definite, but consists of mixtures of numerous chemical compounds in varying amounts. No single bitumen or pitch has been completely separated into its constituent compounds, though, of course, the composition of coal tar is to a great extent known.

According to Abraham,⁸⁰ the element nitrogen is rarely present in excess of 2% of the non-mineral constituents of a bituminous substance. Asphalt, asphaltites and pyrobitumens contain varying amounts, up to a maximum of about 1.7%, of nitrogen, and tars and pitches, except fatty acid pitches, may contain up to 1% of nitrogen.

The amount of sulphur in bituminous substances such as native asphalts, asphaltites and asphaltic pyrobitumens may vary from 0 to 10%, but sulphur compounds are practically absent from all the pyrogenous pitches, *i.e.*, those from wood tar, fatty acids, coal tar.

According to the investigations of O. C. Ralston,⁸⁸ the percentages of carbon, hydrogen and oxygen in bituminous compounds appear to follow some well-defined laws.

For fuller information on the chemical structure, properties, reactions and physical constants and general characters of the various hydrocarbons, oxygen-containing, nitrogenous and sulphur compounds mentioned in this chapter, the reader is referred to any of the well-known standard text-books of organic chemistry.

REFERENCES.

- ⁸⁵ *Industrial and Eng. Chem.*, 1923, 15, 1147. ⁸⁶ *Ibid.*, 1923, 15, 1022.
⁸⁷ *Journ. Oil and Colour Chem. Assoc.*, 1922, 5, No. 35 (cf. Volume on Resins in this series). ⁸⁸ Technical Paper No. 93, U.S. Dept. of the Interior, Bureau of Mines, 1915.

CHAPTER XI

METHODS OF TESTING BITUMINOUS MATERIALS AND PITCHES

American and British Standardisation—Physical, Heat, Solubility and Chemical Tests and their Uses.

THE tests which an investigator will apply to any given material may serve as a means of identification, as a criterion of purity, as an aid to manufacturing control or as an indication of the use to which the material may be applied. In this last-named connection, many of the tests to be applied to a bituminous material or pitch will depend on whether the material is to be used in manufacturing a bituminous varnish or a japan, in preparing a water-proofing material for a damp course or in highway construction.

The standardisation of testing of asphalts, solid and semi-solid bitumens, tars and pitches was undertaken in the United States a very considerable time ago by the American Society for Testing Materials (A.S.T.M.) and very valuable work was achieved. More recently in this country, thanks to the pioneer work of the Institution of Petroleum Technologists, the task of fixing standard tests for Petroleum and its various products has been started and considerable progress has been made. The work of the committee engaged on the task has been reported upon by A. E. Dunstan.⁸⁹ Many of the standard tests of the A.S.T.M. have been recommended for use by this British Committee, who have, however, deferred their decision in the case of many of the tests pending further reports from sub-committees.

The present author in this volume has adopted the tests and the numbers attached thereto as given by Herbert Abraham⁸⁰ in his volume on "Asphalts and Allied Substances," and the reasons that have prompted this course are that many of the tests given are already the adopted standards of the A.S.T.M., and are recommended by the British Committee already referred to. Furthermore, Abraham's scheme of testing is very full and embraces tests adequate for all the industries concerned in the use of bituminous materials and pitches.

In the following pages most of the tests are given only in bare outline, as considerations of space forbid any other treatment, but full description of tests with illustrations of apparatus to be used are given by Spielmann.^{83a} Moreover, it is not the purpose of the present volume to give detailed descriptions of apparatus and technique largely described in the well-known standard works on Chemical Analysis and Experimental Physics.

TABLE XIX.

Tests to be Applied to Bituminous Substances.

Test No.	Description.	Test No.	Description.
	<i>Physical characteristics :</i>		<i>Solubility tests :</i>
Test 1	Colour in mass	Test 21	Solubility in carbon di-sulphide
Test 2	Homogeneity	Test 22	Carbenes
Test 3	Appearance of surface aged one week	Test 23	Solubility in 88° petroleum naphtha
Test 4	Fracture	Test 24	Solubility in other solvents
Test 5	Lustre		
Test 6	Streak on porcelain		<i>Chemical tests :</i>
Test 7	Specific gravity	Test 25	Water
Test 8	Viscosity	Test 26	Carbon
Test 9	Hardness or consistency	Test 27	Hydrogen
Test 9d	Susceptibility factor	Test 28	Sulphur
Test 10	Ductility	Test 29	Nitrogen
Test 11	Tensile strength	Test 30	Oxygen
Test 12	Adhesiveness	Test 31	Free carbon in tars
		Test 32	Naphthalene in tars
	<i>Heat tests :</i>	Test 33	Solid paraffins
Test 13	Odour on heating	Test 34	Saturated hydrocarbons
Test 14	Subjection to heat	Test 35	Sulphonation residue
Test 15	Fusing point	Test 36	Mineral matter
Test 16	Volatile matter	Test 37	Saponifiable constituents
Test 17	Flash point	Test 38	Asphaltic constituents
Test 18	Burning point	Test 39	Unsaponifiable matter
Test 19	Fixed carbon	Test 40	Glycerol
Test 20	Distillation test	Test 41	Diazo reaction
		Test 42	Anthraquinone reaction
		Test 43	Liebermann-Storch reaction
		Test 44	Iodine number

Test 1.—This test calls for no comment, though it is of some use as a means of identification.

Test 2.—Homogeneity of the Material to the unaided Eye at a temperature of 77° F., or when surveyed under the microscope or when melted, are aids to establishing the identity of the material under examination, and serve to show the presence or absence of mineral matter and free carbon.

Test 3.—Appearance of Surface Aged one Week. A small quantity of the bituminous material melted at the lowest possible temperature is, after examination of its surface, covered for a week, to protect it from dust, and then re-examined. If bright and lustrous it will indicate perfect amalgamation of constituents and absence of oily and undissolved constituents—a lustreless surface indicates the contrary.

Test 4.—Fracture may be conchoidal (rounded and curved like a shell), or hackly (irregular and rough), and only hard and brittle substances yield to this test.

Test 5.—Lustre serves as a means of identification—it gives indications of the presence or absence of waxy, greasy constituents.

Test 6.—Streak on Porcelain. This represents the colour of the powder left behind on drawing a piece of the bituminous material across the surface of unglazed porcelain, and the test serves to indicate the use of the material with coloured pigments.

Test 7.—Specific Gravity. This test serves as a means of identification and of figuring the weight of a given volume of the material under test. The test is ascertained by the usual hydrometer, Westphal balance and specific gravity bottle methods, the exact instrument to be used with a given material being conditioned by its nature and consistency.⁹⁰ In this country the standard temperature is 15.5° C. (60° F.) but the A.S.T.M. adopt 77° F.

Test 8.—Viscosity. This test is of use in the examination of materials for road construction. The Engler, Redwood, Saybolt viscosimeters are used in connection with this test, the main use of which is in the examination of liquid and semi-liquid substances for road purposes. The use of these instruments is fully described by B. Redwood, J. Lewkowitsch⁹¹ and others.

For testing the viscosity or consistency of semi-solid bituminous materials for road purposes the Float Test (*Test 8d*) is adopted, and this test is not vitiated by the presence of mineral matter or free carbon.

The instrument as described by Abraham consists of an aluminium saucer-shaped float and a conical brass collar weighing exactly 50 grams together. The brass collar is fitted with melted bituminous material upon placing it against a brass plate, the surface of which has been amalgamated with mercury. After cooling it is levelled, placed in water at 41° F. for 15—30 minutes along with the aluminium float, and then screwed into the float and immediately floated on the surface of water warmed to a desired temperature, with the brass collar downward. Very soft materials are tested at 32° F. and hard bituminous substances at 122° or 150° F. As the heat is transmitted through the brass collar into the plug of bituminous material, the latter softens until it is forced upwards and out of the collar by the weight of the instrument. The time elapsing between the placing of the float on the surface of the water, and when the water breaks through the plug, is taken as a measure of the viscosity of the material under test.

Test 9.—Hardness or Consistency. This is largely a test employed in connection with road-making and pavement bituminous materials, and detailed reference to these tests is out of place in the present volume. The familiar Moh's Hardness Scale is used to some extent, but the Needle Penetrometer^{92, 93, 94} measures the "Penetration, which is defined as the consistency of a bituminous material, expressed as the distance (usually in hundredths of 1 cm.), that a standard needle vertically penetrates a sample of the material under known conditions of loading (usually 100 grams), time (usually 5 seconds) and temperature (usually 77° F.)." A full description of this apparatus, together with an allied one, the Consistometer, is given by Abraham. The Susceptibility Factor (*Test 9d*) is a numerical expression representing the susceptibility of a bituminous substance to temperature changes. It is calculated from the consistometer hardness and fusing point (K. and S.) thus:

$$\text{Susceptibility} = \frac{(\text{Hardness at } 32^{\circ} \text{ F.}) - (\text{Hardness at } 115^{\circ})}{\text{Fusing Point (K. and S.)}} \times 100,$$

and is obviously purely an empirical relationship. Usually this factor is under 40 for blown petroleum asphalts and fatty acid pitches, between 40 and 60 for residual asphalts, and over 60 for tar pitches and asphaltites.

Tests 10, 11, 12.—Ductility, Tensile Strength and Adhesiveness have the physical significance ordinarily attached to these terms, and the tests are mainly of interest in testing road-making bituminous materials.

Heat Tests.

Test 13.—Odour on Heating. Most of the manufactured residual pitches may be recognised by characteristic odours emitted on heating.

Test 14.—Subjection to Heat. A study of behaviour on melting and heating in a flame is often a valuable guide to identification. Many bituminous materials, especially those of low susceptibility factor, melt sluggishly and have an intermediate pasty stage before reaching complete liquidity; noticeably is this the case with blown petroleum asphalts and many fatty acid pitches.

Test 15.—Fusing or Melting Point. The determination of this point raises much controversy from the fact that in strict scientific parlance the term is somewhat of a misnomer when applied to the complex mixture of fatty acids, hydrocarbons, asphaltic, resinous and other compounds which may constitute a bituminous material;

such a substance cannot have a definite melting point, but on heating it passes more or less gradually from hardness through all stages of plasticity to complete liquidity, and the actual temperature recorded as the m. p. or f. p. is that at which the material is sufficiently soft to flow.

A somewhat elaborate method has been devised by G. Kramer and C. Sarnow⁹⁵ (K. and S. method), and modified and elaborated by H. Abraham.⁹³ A method called the Cube Method (Test 15c) has been applied to tar-pitches,⁹⁶ and a modification of this, due to W. Mansbridge,⁹⁷ is preferred for all ordinary purposes by the present author and is carried out as follows. The material to be tested is attached to the bulb of a thermometer, by slightly softening until it adheres, about 6 grams of the pitch or bituminous material, which should cover one-third of the bulb being used. The thermometer is then arranged in a boiling tube (1 in. by 7 ins.), which is fitted into a glass enclosure itself immersed in a small oil-bath, which latter is heated over a small Bunsen flame to give a temperature rise of 2° C. per minute. The thermometer passes through a cork, which closes the tube and is so supported that the bottom of the bulb is 1½ ins. from the bottom of the tube. The temperature at which the bituminous material has softened sufficiently to fall to the bottom of the tube is recorded as the m. p. of the material.

Test 16.—Volatile Matter. This serves to identify various bituminous materials. The A.S.T.M. recommends to heat at 325° F. 50 grams of water-free substance in a flat-bottomed dish 55 min. by 35 mm. for 5 hours in a previously heated oven.⁹⁸

Test 17.—Flash Point. The value of this test is mainly as a criterion of fire risk. The Pensky-Martens Closed Tester is one of the most generally favoured types of tester in this country. Its use is admirably described in any of the standard volumes on technical chemical analysis, and particularly by Redwood.

Test 18.—Burning Point. This test is supplementary to the previous one. The cover of the flash-point tester is removed and the heating and exposure to the test-flame are continued until the vapours ignite and continue to burn.

Test 19.—Fixed Carbon. This test is usually of value with natural asphaltine products, and is carried out as follows:⁹⁹ place 1 gram of the material in a platinum crucible of 20—30 grams weight having a tightly-fitting cover, and heat for exactly 7 minutes by means of a Bunsen flame 20 cm. high, the mouth of the burner being 6—8 cm. below the bottom of the crucible.

Cool and weigh. Remove the cover of the crucible and ignite over a full Bunsen flame until only ash remains. The weight of the first residue less the weight of ash gives the weight of fixed carbon, which should be calculated to a percentage.

Test 20.—Distillation Test. As this is generally a test applied to tars, and particularly in connection with road work, the reader is referred to any of the well-known works on tar or petroleum distillation.

Test 21.—Solubility in Carbon Disulphide. This is often a basis of purchase of bituminous material. The bituminous material should be freed from moisture and 1—2 grams weighed into a 150 c.c. Erlenmeyer flask and agitated with 100 c.c. of carbon disulphide. Filtration removes the insoluble matter. The exact procedure to be adopted is outlined in any of the standard works on analysis. The insoluble matter remaining includes both the non-mineral matter insoluble in carbon disulphide (*Test 21b*) and the mineral matter (*21c*). The former is determined by ignition in a Gooch crucible, and the residue represents the mineral matter.

Test 22.—Carbenes—the bituminous substances soluble in carbon disulphide, but insoluble in carbon tetrachloride.¹⁰⁰ Carbenes¹⁰¹ are found in tar and pitches and in certain hard asphalts and asphaltites, but should not occur in petroleum asphalts to an extent in excess of 0.5%. The procedure is as in *Test 21*, replacing the carbon disulphide by carbon tetrachloride.

Test 23.—Solubility in 88° Petroleum Naphtha. The method is performed in the same manner as for determining the portion soluble in carbon disulphide, 88° petroleum naphtha being substituted for the latter.

Generally it happens that the harder the bituminous product the smaller the percentage that will dissolve in 88° naphtha, and this soluble portion is termed “petrolenes” (also “malthenes”), whilst the non-mineral part insoluble in 88° naphtha is termed “asphaltenes.”

Test 24.—This calls for no comment—circumstances will decide the solvent to be used and the condition of extraction.

Chemical Tests.

Test 25.—Water. The test is mainly used for the purpose of dehydrating the material prior to further examination. Its detailed description will be found in standard volumes on analysis and on tar distillation.

Tests 26, 27, 28, 29, 30.—Carbon and hydrogen are estimated by combustion, sulphur by ignition of the material in a Berthelot

type of bomb calorimeter, nitrogen by the Kjeldahl-Gunning¹⁰² method, and oxygen by difference according to the procedure described in any of the well-known works on organic chemical analysis.

Test 31.—Free Carbon in Tars. This is an adaptation of Test 24 suitable for tars and pitches containing free carbon; hot benzol-toluol is the most satisfactory solvent and thorough extraction is necessary. A special apparatus has been devised by H. J. Cary-Curr.¹⁰³

Test 32.—Naphthalene in Tars. The method adopted is that given in any of the well-known volumes on coal tar.

Tests 33, 34, 35 are of lesser importance generally, and as they are mainly for the purpose of comparison, they need not be described here, but the reader is referred to C. Richardson.¹⁰⁴

Test 36.—Mineral Matter. A detailed examination of this, the amount uncombined, the amount combined with non-mineral constituents, the chemical analysis and microscopic examination of the mineral matter are often of importance in connection with the examination of native asphalts.

Test 37.—Saponifiable Constituents. In this connection it is often important to determine in fatty acid pitches, wood tar pitch and rosin pitch the amounts of free fatty acids, lactones and anhydrides, as well as the saponification values. An estimation of fatty and resin acids is also desirable. The usual standard technique described in any of the well-known works on oils and fats is adopted, though it will be found convenient in many cases to use light petroleum spirit as the solvent. For saponification values, the proposal of Marcusson¹⁰⁵ is to be recommended thus: 5 grams of the pitch or other material in 25 c.c. of pure benzol are refluxed for 1 hour with 25 c.c. of normal alcoholic caustic potash solution, and after cooling 200 c.c. of neutralised 96% alcohol are added, and the mixture is titrated with semi-normal hydrochloric acid solution, using as indicators together 3 c.c. of 1% alcoholic phenol phthalein solution and 3 c.c. of 1% alcoholic alkali blue solution, the colour change being from brownish-red to a distinct blue.

Test 38.—Asphaltic Constituents. J. Marcusson¹⁰⁶ has outlined methods for distinguishing between native and petroleum asphalts, and in the detailed scheme of analysis proposed he determines free asphaltous acids, anhydrides, asphaltenes, asphaltic resins and oily constituents.

Test 39.—Unsaponifiable and Saponifiable Matters. This test is of considerable value as a means of identification and as a criterion of quality. The customary methods are applicable after the

bituminous material has first been freed from insoluble constituents by refluxing with benzol.

Test 40.—Glycerol. This test is of special importance in the examination of bituminous paints, japans, etc., as glycerol indicates the presence of triglycerides, which may be present in stearine pitches. The standard method¹⁰⁷ is adopted after the glycerine has been obtained by prior saponification.

Test 41.—Diazo Reaction. This enables phenols to be detected, and is a means of identifying most of the tar pitches. The particular adaptation to be used is that due to E. Graefe.¹⁰⁸

Test 42.—The Anthraquinone Reaction for detecting anthracene in tar products and

Test 43.—Liebermann–Storch Reaction, which serves as a qualitative test for detecting rosin, rosin oil, or cholesterol is the well-known test as described in any standard work on oils and fats.

Test 44.—Iodine Value. According to Pickering¹⁰⁹ and others, this determination is not usually possible, owing to lack of a suitable solvent, but the present author has obtained good results for a great variety of fatty acid pitches. About 0.1 gram of the material is dissolved in 20 c.c. of cold carbon tetrachloride, and this operation may require up to 2 hours. The operation is then proceeded with exactly as for a fatty oil by the method of Wijs. Though the solution is usually very dark, the colour change at the end of the titration is quite definite and unmistakable.

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CHAPTER XII

NATIVE ASPHALTS

Origin and Relationship to other Naturally Occurring Bituminous Bodies—
The Bermudez and Trinidad Pitch Lakes—Composition of Natural
Asphalts.

In considering the origin of deposits of bitumens and pyrobitumens geological considerations are of prime importance, though within the compass of this chapter it is impossible to make more than a passing reference to the subject. Bitumens and pyrobitumens, in all but a few cases, are found in sedimentary deposits of sand, sandstone, limestone and sometimes in shale and clay—only very rarely in igneous rocks.

Bitumens and pyrobitumens are found in nature in the following ways ⁸⁰ :—

1. Overflows :

- (a) Springs—source of petroleum and liquid forms of asphalt.
- (b) Lakes—some of largest deposits of asphalt found in this way.
- (c) Seepages—these occur in the case of petroleum and liquid forms of asphalt, usually cliffs and mountain sides bearing impregnated rock.

2. Impregnated Rocks :

- (a) Subterranean pools or reservoirs—all the large deposits of petroleum occur in this way.
 - (b) Horizontal rock strata
 - (c) Vertical rock strata
- } Liquid and semi-liquid asphalts
} occur in this way.

3. Filling Veins :

- (a) Caused by vertical cleavage
 - (b) Caused by upturning
 - (c) Caused by sliding
 - (d) Formed by sedimentation
- } The harder asphalts, asphalt-
ites and asphaltic pyro-
bitumens are usually found
in fissures as a result of
one or other of these opera-
tions.

Discussion as to the origin of bitumens and related substances has generally centred itself on the origin of petroleum, this being considered the parent substance. Amongst the theories advanced

to account for the origin of petroleum may be cited the one that free metallic elements at high temperatures in the interior of the earth react to produce metallic carbides, which in contact with water produce acetylenes, and these, in turn, by appropriate condensations, give rise to petroleum. W. Ramsay^{110, 111} has commented on the almost universal occurrence of nickel in the ash from petroleum, and concludes that the catalytic reduction of carbon monoxide or carbon dioxide may account for deposits of petroleum.

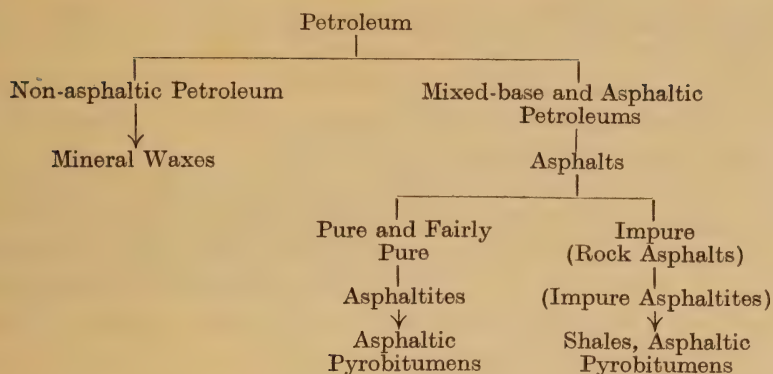
Various organic theories have been advanced purporting to explain the origin of petroleum from decaying vegetable matter, deposits of sea-weeds, etc., and in like manner petroleum and asphalt are considered as possibly derived from accumulations of animal matter and fish, which in time have decomposed into hydrocarbons. In this connection the work of S. Kawai and S. Kobayashi¹¹² on a petroleum-like hydrocarbon derived by heating shark liver oil in contact with dry clay under pressure is interesting. E. H. C. Craig¹¹³ has ably summarised the most important of the recent investigations bearing on this subject.

Notwithstanding the conflicting views as to the origin of petroleum, there is substantial agreement that petroleum, once formed, is gradually converted into other types of bitumens and pyrobitumens, the cumulative influences of time, heat and pressure being important desiderata.

The view currently held is that advanced by Clifford Richardson^{114, 115} after a study of the Trinidad asphalt deposit. Here it is concluded that an asphaltic petroleum existing at a considerable depth is converted into asphalt as a result of surface action in which a thorough emulsification with colloidal clay, sand and water is brought about by the action of natural gas acting under high pressure. During this metamorphosis hydrogen is supposedly eliminated, the hydrocarbons being enriched in carbon thereby, and becoming structurally more complex. In turn harder asphalts, asphaltites and asphaltic pyrobitumens may be formed in a favourable environment.

According to Peckham¹¹⁶ in a review of the chemistry and technology of Californian bitumen and asphalt since 1865, the polymerisation of petroleum and the rapidity of its conversion into asphalt are due largely to the content of unstable compounds of nitrogen and sulphur in the petroleum.

Tentatively one may consider the following series of metamorphoses :



The non-asphaltic pyrobitumens—the lignites, coal shales, bituminous coals and anthracite, are outside the scope of our survey and need not be considered therefore.

We are now in a position briefly to review the more important native asphalts, commencing with those deposits containing less than 10% of mineral matter, and these we may term :

The Pure Native Asphalts.—These are found in various parts of the United States, notably in Utah and California, the deposit in the latter State averaging 85% asphalt, 10% mineral matter and 5% moisture and natural gas. Deposits occur also in Mexico and Cuba, but the most important one is that of Bermudez in Venezuela, the so-called Bermudez Pitch Lake, on the western side of the Gulf of Paria and opposite the Island of Trinidad. The asphalt lake extends over 900 acres in swampy land and averages 4 ft. in depth. Where the asphalt exudes from the springs it is quite soft, but the surface of the deposit hardens slowly on exposure and at the edge of the lake the asphalt is hard and brittle.

According to Richardson¹⁰⁴ the dried crude Bermudez asphalt has the following characteristics :

(Test 1)	Colour in mass	Black
(Test 4)	Fracture	Conchoidal
(Test 5)	Lustre	Bright
(Test 7)	Specific gravity at 77° F.	1.005—1.075
(Test 15 <i>d</i>)	Temperature at which it flows	135—188° F.
(Test 16)	Volatile at 400° F. in 7 hrs. (dried material)	5.81—16.05%
(Test 21 <i>a</i>)	Soluble in carbon disulphide	90—98%
(Test 21 <i>b</i>)	Non-mineral matter insoluble	0.62—6.45%
(Test 21 <i>c</i>)	Free mineral matter	0.50—3.65%

The water present with this asphalt is not emulsified with the asphalt, as is the case with the Trinidad deposit to be described later. The amount of water varies from 10 to 40%. For a full

description of the refined Bermudez asphalt the reader must consult Bardwell.^{117, 118}

Other similar deposits are the La Brea deposit in the delta of the River Orinoco and small deposits in France, Greece, Eastern Siberia and the Philippine Islands.

Native Asphalts associated with Mineral Matter.—Deposits are found in Kentucky, composed of sand and sandstones with 4—12% of asphalt, whilst in the State of Oklahoma are some of the richest asphalt deposits in the U.S.A. Here the deposits are found in both liquid and solid forms, and most of what is mined is used for paving purposes. The crude rock is boiled with water, the impure asphalt rising to the surface and the sand waste settling to the bottom.

Other deposits occur in Texas, Utah and California, at Alberta in Canada, in Mexico and Cuba. The largest deposit in the world, however, is that known as the "Trinidad Asphalt Lake," near the village of La Brea in Trinidad. This deposit covers an area of 115 acres to an average (estimated) depth of 150 ft. in the centre, where it is undoubtedly fed by gradual seepage from below, as the level of the lake has dropped only very slightly in spite of the removal of vast quantities of the asphalt for use in pavement construction.

The crude asphalt is an emulsion of bituminous matter, water and finely divided mineral matter, and is very constant in composition. There is naturally some slight change in character, as the asphalt gradually flows from the centre of the lake, where it is softest, to the edges, where it becomes harder. P. Carmody¹¹⁹ gives the following data :

	Water.	Ash.	Bitumen.	Other organic matter.
Soft	29.04%	24.1%	45.6%	1.24%
Hard ...	21.4—27.4%	27.4—29.7%	40.2—42.0%	4.4—5.0%

Samples, after pulverising and drying at ordinary temperatures, show about 55% of bituminous matter soluble in carbon disulphide, and about 35% of mineral matter, the balance being water of hydration, bituminous matter adsorbed by the clay, and thus rendered insoluble in carbon disulphide.

The bituminous matter of the "lake asphalt" is a true asphalt, as distinct from the asphaltites and pyrobitumens. The crude

asphalt differs only from a residual asphalt made by the distillation of a crude oil in respect to its large content of mineral matter and relatively high content of sulphur, 2—10%, usually in excess of 4%.

From one edge of the lake there is a gradual steady movement of asphalt towards the sea. The asphalt from this flowing sheet is locally known as "land asphalt," and is not so uniform in composition and differs somewhat from the "lake asphalt." Carmody (*loc. cit.*) gives the following examples :

	Soft lake asphalt.	Hard lake asphalt.	Land asphalt.	Asphalt from seashore.
	%	%	%	%
Volatile matter	54.5	53.3	47.7	33.7
Fixed carbon	9.6	10.3	9.8	8.0
Ash	5.7	5.2	4.8	4.2
Asphaltenes	14.7	16.7	10.4	7.9
Total organic to 100 parts inorganic	207.6	180.7	170.1	79.7

The crude asphalt is refined by heating to about 160° C. to remove water, mechanical impurities being at the same time skimmed off or settled out.

The refined asphalt, the so-called Trinidad *épuré*, has the following properties :

Specific gravity at 25° C.	About 1.40
Conchoidal fracture and dull lustre.	
Penetration (Dow) at 25° C.	About 7
Ductility (Dow) at 25° C.	" 2
Melting point (K. & S.)	" 87° C.
Bituminous matter, soluble in carbon disulphide ...	" 57%
Mineral matter	" 38%
Melting point of the pure bituminous matter, free from mineral matter	" 55° C.
Ultimate analysis of the bituminous material	$\left. \begin{array}{l} \text{C. } 80-82\% \\ \text{H. } 10-11\% \\ \text{S. } 6-8\% \\ \text{N. about } 0.8\% \end{array} \right\}$

Solubility of the pure bituminous matter upon extraction cold by :

Acetone	21.7%
Benzol	99.9%
Chloroform	93.4%
Ethyl ether	68.9%

Native asphalts of lesser importance occur also in France, Switzerland, Germany, Austria, Italy, Spain, Russia, Syria, Iraq, Algeria and deposits of bituminous marl in Ismid, Asia Minor.¹²⁰

Comparatively recently further light has been thrown on the chemical composition of the natural asphalts by the researches of Marcusson,^{121, 122} and he subdivides these bodies into four main classes :

1. Oily substances, in the main saturated and unsaturated hydrocarbons.

2. Petroleum resins, or "Petrolenes," which form the first stage of conversion of petroleum hydrocarbons into asphaltenes. They are brownish-black masses soluble in petroleum spirit, chloroform and carbon disulphide.

3. "Asphaltenes," formed by the action of oxygen or sulphur on the resins, or by intramolecular change in these. The bodies are completely soluble in carbon disulphide, benzol and chloroform, and contain 7—13% sulphur. These and the parent resins appear to be saturated polynuclear compounds containing oxygen or sulphur.

4. Asphaltogenic acids, and their anhydrides—tar-like or resinous masses soluble in chloroform and ethyl alcohol.

The following table is instructive :

TABLE XX.

Marcusson's Subdivision of Asphalts.

	Free asphaltogenic acids.	Inner anhydrides.	Asphaltenes.	Petroleum resins.	Oily substance.
Bitumen from Trinidad asphalt	% 6.4	% 3.5	% 37.0	% 23.0	% 31.0
Bermudez asphalt	3.9	2.0	35.3	14.4	39.6

The "petrolenes" of Trinidad asphalt are extremely sticky and of cement-like nature, and not merely oily, and they (the petrolenes) impart to the asphalt its cement-like property. The "asphaltenes" impart cohesiveness as distinguished from adhesiveness, and supply body and stability to the binding material.

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CHAPTER XIII

ASPHALTITES

Gilsonite, Manjak and Grahamite—Their Occurrence and Characteristics—
The Asphaltic Pyrobitumens—Elaterite, Wurtzilite, Albertite, Impsonite.

ASPHALTITES are naturally occurring asphalt-like substances characterised by high melting points (over 250° F.), and Abraham recommends the following means of differentiating their three main classes—gilsonite, glance pitch, and grahamite—one from the other, as follows :

	Streak.	Specific gravity at 77° F.	Fusibility (K. & S.) ° F.	Fixed carbon. %
Gilsonite or uintaite	Brown	1.05—1.10	250—350	10—20
Glance pitch or manjak * ...	Black	1.10—1.15	250—350	20—30
Grahamite *	Black	1.15—1.20	350—600	30—35

* When substantially free from mineral matter.

In all three classes the non-mineral constituents are almost completely soluble in carbon disulphide.

These bitumens are rather narrowly distributed in nature and are considered by Richardson ^{123, 124} to be the result of metamorphic changes in petroleum under a particular environment. From the softest gilsonite, which will flow slowly on exposure, to the hardest grahamite not melting even at high temperatures, are materials of varying consistency. A hardening in consistency is accompanied by gradual decrease in the percentage amount of the material soluble in petroleum spirit or naphtha and an increase in the yield of residual coke. These differences become the more striking when comparison is made with other petroleum derivatives, as shown in the following table due to Richardson : ¹²⁵

TABLE XXI.

Comparison of some Petroleum Derivatives.

	Specific gravity at 77° F.	Sol. in naphtha. %	Saturated hydrocarbon. %
Petroleum flux (Texas)	0.956	97.5	72.8
Petroleum residual pitch	1.089	65.0	33.1
Bermudez asphalt	1.082	62.2	24.4
Gilsonite (Utah)	1.044	47.7	5.5
Grahamite (Oklahoma)	1.171	0.4	0.3

The relations in composition of gilsonite, grahamite and other forms of natural bitumen have been tabulated in a paper by Mabery.¹²⁶

Gilsonite.—This is found only in one region extending from the eastern portion of the State of Utah into the western portion of Colorado, and occurs in parallel vertical veins from a fraction of an inch in thickness to a width of 18 ft. The material is removed by a crude mode of mining.

A sample examined by the present author⁸⁴ some time ago had the following characters :

Colour in mass	Jet black
Fracture	Conchoidal, the sample being very brittle
Lustre	Very bright
Ash	Only 0.75%
Solubility in carbon disulphide	99.75%
Melting point (drop method)	130° C.
Saponifiable matter	Nil

According to Abraham,⁸⁰ *gilsonite* is fairly uniform in composition and complies with the following characteristics :

(Test 1) Colour mass	Black
(Test 4) Fracture	Conchoidal
(Test 5) Lustre	Bright to fairly bright
(Test 6) Streak	Brown
(Test 7) Specific gravity at 77° F.	1.05—1.10
(Test 9a) Hardness on Moh's scale	2
(Test 9b) Hardness, needle penetrometer at 77° F. .	0
(Test 9c) Hardness, consistometer at 115° F.	40—60
Hardness, consistometer at 77° F.	90—120
Hardness, consistometer at 32° F.	Too hard for test
(Test 9d) Susceptibility factor	>100
(Test 10a) Ductility at 77° F. (Author's method)	0
(Test 13) Odour on heating	Characteristic
(Test 14a) Behaviour on melting	Forms a comparatively thick, viscous melt
(Test 14b) Behaviour on heating in flame	Softens and flows
(Test 15a) Fusing point(K. & S. method)	250—350° F.
(Test 15b) Fusing point (Ball and ring method)	270—370° F.
(Test 16) Volatile at 325° F. 7 hours (dry substance)	Less than 2%
Volatile at 400° F. 7 hours	Less than 4%
Volatile at 500° F. 4 hours	Less than 5%
(Test 19) Fixed carbon	10—20%
(Test 20) Distillation test.	
0—150° C.	9.34% Distillate
150—200° C.	5.35% Distillate
200—250° C.	12.84% Distillate
250—300° C.	28.99% Distillate
Above 300° C.	Coked
(Test 21a) Soluble in carbon disulphide	Greater than 98%
(Test 21b) Non-mineral matter insoluble	0—1%
(Test 21c) Mineral matter	Trace—1%

(Test 22)	Carbenes	0— $\frac{1}{2}$ %
(Test 23)	Soluble in 88° naphtha	40—60%
(Test 24)	Grams soluble in 100 grams of cold solvent :—	
	Amyl acetate	86
	Amyl alcohol	Insoluble
	Amyl nitrate	51
	Aniline	Insoluble
	Benzol	71
	Carbon disulphide	Soluble in all proportions
	Carbon tetrachloride	44
	Chloroform	54
	Ethyl acetate	3
	Ethyl alcohol	Insoluble
	Ethyl ether	Soluble in all proportions
	Naphtha 62°	5
	Nitrobenzene	9
	Propyl alcohol	Insoluble
	Toluol	72
	Turpentine	60
(Test 26)	Carbon	88—89.5 %
(Test 27)	Hydrogen	8.5—10.0 %
(Test 28)	Sulphur	1.7—2.0 %
(Test 29)	Nitrogen	0.8%
(Test 30)	Oxygen	0—2%
(Test 33)	Paraffin scale	0—Trace %
(Test 35)	Sulphonation residue	85—95%
(Test 37)	Saponifiable matter	Trace
(Test 41)	Diazo reaction	No
(Test 42)	Anthraquinone reaction	No

Glance Pitch.—This resembles gilsonite in external appearance. It always shows a brilliant conchoidal fracture. It occurs in Mexico, Colombia (S. America), Syria and in the West Indies. That occurring in Barbados is generally marketed under the name of Barbados “Manjak”¹²⁷ It is claimed that no other native bitumen equals it in respect of its lustre, strength, melting point, intensity of colour and elasticity.

According to Abraham, this “manjak” contains sulphur 0.7—0.9%, 1 to 2% mineral matter, specific gravity at 77° F. about 1.10, fusing point 320—340° F. (K. & S. method), fixed carbon 25—30%, and 97—98% of the bitumen is soluble in carbon disulphide.

R. H. Emtage¹²⁸ also quotes the following analysis for Barbados “manjak”—carbon 83.62%, oxygen and nitrogen 2.05%, hydrogen 8.29%, sulphur 0.85%. Water to the extent of 2.49% and ash 2.70% are recorded.

According to Abraham,⁸⁰ Glance Pitch complies with the following characteristics :

(Test 1)	Colour in mass	Black
(Test 4)	Fracture	Conchoidal to hackly

(Test 5) Lustre	Bright to fairly bright
(Test 6) Streak on porcelain	Black
(Test 7) Specific gravity at 77° F.	1.10—1.15
(Test 9a) Hardness, Moh's scale	2
(Test 9b) Hardness, needle penetrometer at 77° F. .	0
(Test 9c) Hardness, consistometer at 77° F.	90—120
(Test 9d) Susceptibility factor	>100
(Test 10) Ductility at 77° F.	0
(Test 13) Odour on heating	Asphaltic
(Test 14a) Behaviour on melting	Forms a comparatively thick and viscous melt
(Test 14b) Behaviour on heating in flame	Softens and flows
(Test 15a) Fusing point (K. & S. method)	250—350° F.
(Test 15b) Fusing point (Ball and ring method)	270—375° F.
(Test 16) Volatile at 325° F. 7 hours (dry substance)	Less than 2%
(Test 16) Volatile at 400° F. 7 hours	Less than 4%
(Test 19) Fixed carbon	20—30%
(Test 21a) Soluble in carbon disulphide	Usually greater than 95%
(Test 21b) Non-mineral matter insoluble	Less than 1%
(Test 21c) Mineral matter	Less than 5%
(Test 22) Carbenes	Less than 1%
(Test 23) Soluble in 88° naphtha	20—50%
(Test 26) Carbon	80—85%
(Test 27) Hydrogen	7—12%
(Test 28) Sulphur	2—8%
(Test 29) Nitrogen and oxygen	A trace to 2%
(Test 33) Paraffin	0—trace %
(Test 35) Sulphonation residue	80—95%
(Test 37) Saponifiable matter	Trace
(Test 41) Diazo reaction	No
(Test 42) Anthraquinone reaction	No

Grahamite.—This asphaltite may be very pure or may be associated with as much as 50% of mineral matter. It occurs in West Virginia, Oklahoma, Colorado, Mexico and Cuba. It is found in veins of varying thickness from which it is mined.

A number of veins of grahamite are mined also in the island of Trinidad, and near San Fernando, on the west coast of the island, occur deposits of the so-called “manjak.” Its properties are as follows :

Specific gravity at 25° C.	About 1.17
Melting point (K. & S.)	175—225° C.
Fixed carbon	About 33%
Soluble in carbon disulphide	92—96%
” ” tetrachloride	About 54%
” petroleum ether 88° Be	13—18%

The largest vein is that worked at the Vistabella mine. The composition of the product throughout this vein is not constant; at the edge the manjak is amorphous or coal-like in character; at the centre it is lustrous and like gilsonite in appearance. The melting point of this latter type is lower and its solubility in

petroleum ether,—viz., about 55%—is much greater. The distillation test is as follows :

Below 150° C.	0.5%
150—300° C.	26.5%
Above 300° C.	18.0%
Carbonaceous residue	55.0%

This “manjak” yields on extraction with acetone and subsequently with chloroform 12.06% of “petrolenes” and 83.19% of “asphaltenes” with 4.75% of insoluble residue.¹²⁹

Grahamite, in general, according to Abraham⁸⁰ complies with the following :

(Test 1) Colour in mass	Black
(Test 4) Fracture	Conchoidal to hackly
(Test 5) Lustre	Very bright to dull
(Test 6) Streak on porcelain	Black
(Test 7) Specific gravity at 77° F. :—	
Pure varieties (containing less than 10% mineral matter)	1.15—1.20
Impure varieties (containing more than 10% mineral matter)	1.175—1.50
(Test 9a) Hardness (Moh's scale)	2—3
(Test 9b) Hardness needle penetrometer at 77° F. ...	0
(Test 9c) Hardness, consistometer at 77° F.	Over 150
(Test 9d) Susceptibility factor	100
(Test 14b) Behaviour on heating in flame :—	
Variety showing a conchoidal fracture and a black lustre	Decrepitates violently
Variety showing a hackly fracture and a fairly bright to dull lustre	Softens, splits and burns
(Test 15a) Fusing point (K. & S. method)	350—600° F.
(Test 15b) Fusing point (Ball and ring method)	370—625° F.
(Test 16) Volatile at 500° F. 4 hours	Less than 1%
(Test 19) Fixed carbon	30—55%
(Test 21a) Soluble in carbon disulphide	45—100%
(Test 21b) Non-mineral matter insoluble in carbon disulphide	Less than 5%
(Test 21c) Mineral matter	Variable (up to 50%)
(Test 22) Carbenes	0—80%
(Test 23) Soluble in 88° petroleum naphtha	Trace to 50%
(Test 30) Oxygen in non-mineral matter	0—2%
(Test 33) Paraffin	0 to trace %
(Test 35) Sulphonation residue	80—95%
(Test 37) Saponifiable matter	Trace
(Test 41) Diazo reaction	No
(Test 42) Anthraquinone reaction	No

In general, grahamite is characterised by the following features :

1. High specific gravity ;
2. Black streak ;
3. High fusing point ;
4. High percentage of fixed carbon ;
5. Solubility of non-mineral matter in carbon disulphide.

Asphaltic Pyrobitumens.—These are naturally occurring substances composed of hydrocarbons characterised by their infusibility and comparative freedom from oxygenated substances. The principal classes, usually containing less than 10% of associated mineral matter, are as follows :

	Streak.	Specific gravity at 77° F.	Fixed carbon. %
Elaterite	Light brown	0.90—1.05	2—5
Wurtzilite	Light brown	1.05—1.07	5—25
Albertite	Brown to black	1.07—1.10	25—50
Impsonite	Black	1.10—1.25	50—85

All these are results of petroleum metamorphosis.

Elaterite is found in England, Australia and near L. Balkash and has little beyond scientific interest. It was discovered in Derbyshire in 1673,¹³⁰ is moderately soft and elastic, contains 6—7% ash and is slightly soluble in ether.

Wurtzilite is found only in Utah,¹³¹ occurring there in veins of varying width and length. It is characterised by being sectile and cutting like horn; if bent too far or suddenly it snaps. Its principal tests are quoted by Abraham as follows :

Colour in mass	Black
Specific gravity at 77° F.	1.05—1.07
Hardness, consistometer, 77° F.	Over 150

(On heating in a flame it softens and burns quietly, but does not fuse without decomposition.)

Fixed carbon	5—25%
Mineral matter	0.2—2.5%
Soluble in CS ₂	5—10%
Carbon	About 80%
Hydrogen	10—12%
Sulphur	4—6%
Nitrogen	About 2%

Albertite occurs in New Brunswick, Nova Scotia, Utah, Tasmania and in West Africa. It is characterised by its infusibility, insolubility in carbon disulphide, specific gravity (1.07—1.10 at 77° F.), fixed carbon 25—50% and small percentage of oxygen (less than 3%). At one time this product was utilised to enrich bituminous coal in the manufacture of coal gas.

Impsonite represents the final stage in the metamorphosis of asphaltites and asphaltic pyrobitumens. It is characterised by its infusibility and insolubility in carbon disulphide and comparatively small percentage of oxygen (less than 5%).

The most important deposits are found in Oklahoma, Arkansas, Nevada.

Somewhat allied are the asphaltic pyrobituminous shales and the non-asphaltic pyrobituminous shales, in the latter of which are associated the cannel coals, torbanites and pyropissite. For further information on these latter substances the reader is referred to the publications of Watson Smith,¹³² Baskerville and Hamor¹³³ and others.

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CHAPTER XIV

PETROLEUM ASPHALTS, OR RESIDUAL PITCHES

Occurrence, World's Production, and Refining of Petroleum—Characteristics of Residual, Blown and Sulphurised Petroleum Asphalts.

VERY closely allied to the native asphalts are the residuals from the distillation of petroleum, not only by reason of similarity in appearance and in chemical composition, but in virtue of similarity of applicability. These petroleum asphalts are jet-black shining solids, often brittle and usually showing a conchoidal fracture, having a low ash content, usually about 0.1%. With the exception of the Mexican residuals, they contain only small amounts of sulphur, so that in these two latter respects they are in marked contrast to the native asphalts.

Petroleum occurs in different parts of the world, and varies widely in composition. The extent of its production is shown in a table recently prepared by Mr. George Sell, published in a paper on "Crude Oils of the Empire" ¹³⁴ (see Table XXII, p. 106).

From the standpoint of this chapter, petroleum may be divided into three groups :

1. Those bearing a substantial quantity of solid paraffins, usually associated with open chain hydrocarbons.
2. Those bearing a substantial proportion of asphaltic bodies, usually associated with cyclic hydrocarbons.
3. Those of mixed composition, bearing both solid paraffins and asphaltic bodies.

Paraffinoid hydrocarbons predominate in the petroleum produced in Pennsylvania, West Virginia, Lima (Ohio), Canada and Alaska, and the residues do not yield asphalts on distillation.

Mixed base petroleum covering both asphalts and paraffins occur in Illinois, Texas, Mexico and Roumania.

Cyclic hydrocarbons predominate in petroleum produced in the Mexican Gulf field, California, Trinidad, and these fields yield asphaltic petroleum. In the case of the Borneo field, some of the petroleum here is asphaltic, whilst some has a paraffin base. The Baku field gives a petroleum in which the cyclic hydrocarbons of the C_nH_{2n} series—the naphthenes—predominate, though the oil is not asphaltic.

After dehydration crude petroleum is fractionally distilled, the process being intermittent or continuous, and both methods are employed either with or without steam : in the latter case the distillation is said to be dry.

TABLE XXII.

World's Production of Petroleum. (In Imperial gallons.)

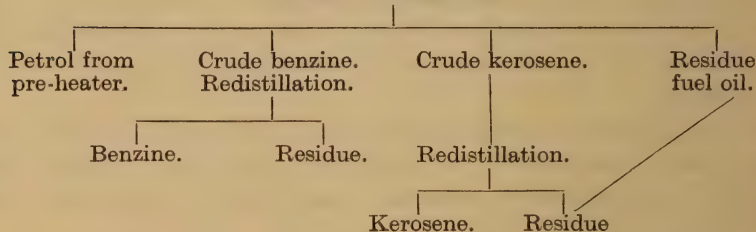
Country.	1920.	1921.	1922.	1923. Estimated or based on preliminary returns.
United States	15,519,070,000	16,526,305,000	19,513,585,000	25,399,570,000
Mexico	6,103,089,600	6,460,129,200	6,370,000,000	5,233,544,000
Russia	907,500,000	924,000,000	1,209,000,000	1,344,000,000
Eastern Archipelago	585,541,500	588,464,400	585,189,000	583,000,000
Persia	394,703,100	505,660,500	665,081,700	846,487,700
Roumania...	263,875,300	301,846,100	354,678,700	391,340,400
Galicia.....	196,062,200	180,694,400	182,804,200	188,831,000
Peru	98,582,700	125,000,000	127,000,000	128,000,000
Japan and Formosa ...	93,205,000	91,000,000	90,000,000	88,000,000
Argentina ...	50,963,600	51,247,500	71,087,400	80,000,000
Venezuela ...	17,360,000	50,000,000	70,000,000	100,000,000
France	13,601,800	13,766,500	19,101,000	17,511,900
Germany.....	8,418,700	9,000,000	11,000,000	13,000,000
Italy	1,360,500	1,317,300	1,300,000	1,300,000
British Empire—				
India	293,116,800	305,683,200	298,504,100	298,000,000
Trinidad ...	72,906,000	82,395,600	85,566,300	90,000,000
Egypt	37,281,100	51,376,000	45,000,000	35,000,000
Sarawak ...	35,138,100	49,632,200	100,178,900	135,000,000
Canada	6,868,800	6,563,900	6,267,400	6,160,000
United Kingdom.	102,100	91,400	32,800	7,500
Total ...	24,698,746,900	26,324,173,200	29,805,376,500	34,978,752,500

Figures in black are estimated.

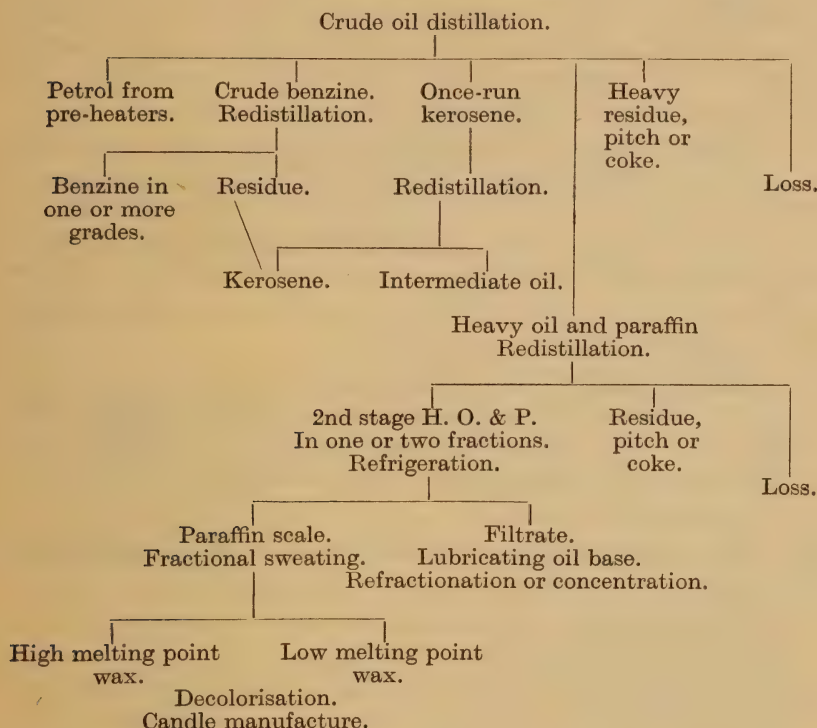
For full details as to the operation of petroleum distillation the reader must have recourse to the works of Redwood ¹³⁵ and Campbell, ¹³⁶ but in bare outline two refining schemes may be quoted, due to A. E. Dunstan and J. Kewley: ¹³⁴

Topping Scheme.

Crude oil distillation.



Full Refining Scheme.



The main refinery products are given in Table XXIII below : ¹³⁴

TABLE XXIII

Principal Refinery Products from Crude Petroleum.

Name.	Specific gravity range.	Initial and final boiling points, ° C.	Remarks.
Naphtha } Benzine	{ 0.728—0.759	95—150	—
Gasoline }	{ 0.639—0.780	31—190	—
Kerosene	0.785—0.811	140—310	—
Gas-oil	0.816—0.855	300—350	—
Fuel-oil	0.85 —0.96	300 and upwards	Not more than 1% of sulphur.
Lubricating oil	0.882—0.905	300 and upwards	Free from sulphur and asphalt.
Residual oil	0.928—0.96	—	—

The residual products obtained in the distillation of petroleum are represented by the following classes, according to Abraham :

(a) *Residual Oil*.—The residue from the dry-distillation of paraffinoid petroleum, the steam or the dry distillation of mixed-base petroleum and the steam distillation of asphalt-bearing petroleum. This residual, termed liquid asphalt, petroleum flux, etc., is liquid or semi-liquid at the ordinary temperature.

(b) *Residual Asphalt*.—The residue from steam or dry distillation of mixed base and the steam distillation of asphalt-bearing petroleum.

(c) *Blown Asphalts*.—The products obtained by blowing air through residual oils at high temperature.

(d) *Sulphurised Asphalt*.—A product obtained by heating residual asphalt with sulphur at high temperature.

(e) *Sludge Asphalt*.—The asphalt-like body separated from the acid sludge produced in the refining of petroleum distillates with sulphuric acid. The newer methods of refining petroleum will doubtless eventually eliminate this type of residual.

(f) *Petrolatum or Vaseline*.

The following yields are obtained from a California asphaltic petroleum : 137

Gasoline (60° Bé.)	Trace—20%
Naphtha (55° Bé.)	Trace—15%
Kerosene (35—42° Bé.)	Trace—30%
Gas or fuel oil (25—30° Bé.)	10—40%
Lubricating oil (17—25° Bé.)	15—70%
Residual asphalt	20—40%
Loss	1—4%

The characteristics of residuals depend on the following factors :

(a) The nature of the petroleum from which they are derived.

b) The extent to which the distillation is carried.

(c) The method of distillation employed and the care with which the operation is conducted have some bearing on the result also.

Residual asphalts in general comply with the following characteristics given in a table due to Abraham :

(Test 1)	Colour in mass	Black
(Test 2)	Homogeneity	Variable
(Test 4)	Fracture	Conchoidal in case of hard residues
(Test 6)	Streak on porcelain	Black
(Test 7)	Specific gravity at 77° F.	1.00—1.17
(Test 9b)	Penetration at 77° F.	150—0
(Test 9c)	Consistency at 77° F.	5—100
(Test 9d)	Susceptibility factor	40—60
(Test 11)	Tensile strength at 77° F.	0.5—10.0
(Test 15a)	Fusing point (K. & S.)	80—225° F.
(Test 17)	Flash point	400—600° F.
(Test 18)	Burning point	450—700° F.

(Test 19)	Fixed carbon	5—40%
(Test 21a)	Soluble in carbon disulphide	85—100%
(Test 21c)	Mineral matter	0—1%
(Test 23)	Solubility in 88° naphtha	25—85%
	Carbon 85—87%, Hydrogen 9—13%, Sulphur trace —10%, Nitrogen trace —1%, Oxygen 0—2.5%	
	Saponifiable constituents	0—2%

Some petroleum residual pitches examined by the present author⁸⁴ showed the following characters :—

	Specific gravity at 15.5° C.	M. p. (° C.).	Ash. %
Residual pitch from—			
An American petroleum I .	1.045	82—83	0.07
" " " II .	1.060	110	0.08
A Mexican petroleum	1.001	122	0.12
An Asiatic "	1.107	65—67	0.72

None showed more than a trace of saponifiable matter, and except in the case of the Mexican variety, sulphur was present only in trace.

According to Marcusson,¹³⁸ petroleum residual asphalts or pitches do not contain asphaltogenic acids, and the proportion of oily constituents (and their characteristics) depends on the extent of the distillation, but the amount is much greater than in the natural asphalts. The residues from some of the American petroleums contain notable quantities of aromatic hydrocarbons, such as anthracene, phenanthrene, chrysene and pyrene. Further, these residual asphalts are insoluble in water, acids, alkalies and only slightly soluble in alcohol, though readily soluble in benzol and carbon disulphide.

Blown Residual Asphalts.

Air-blown asphalts derived from residual oils derived in turn from asphaltic mixed base or non-asphaltic petroleums have been manufactured for many years since they were first reported upon by Gesner in 1865, and the first commercial scale operation was brought about by F. X. Byerley in 1894.¹³⁹ Generally, air and steam are blown into the residual oils at 270—300° C. for 10 to 24 hours. The advantages of "blowing" over steam distillation are that it is easier to produce an asphalt of a particular grade and of better quality, and, in addition, the asphalt acquires a somewhat rubber-like property. Moreover, the yield of asphaltic residue from "blowing" is greater than by steam distillation.

What the chemical changes are during blowing is uncertain, but D. Holde and S. Weill¹⁴⁰ have examined some of these blown asphalts, and find their saponification values increase with rise of melting point. In general, blown asphalts comply with the following characteristics: ⁸⁰

(Test 1)	Colour in mass	Black
(Test 2a)	Homogeneity to the eye at room temperature	Uniform to gritty
(Test 2b)	Homogeneity under the microscope	Uniform to lumpy
(Test 3)	Appearance surface aged indoors one week	Bright to dull and greasy
(Test 4)	Fracture	Soft grades do not show a fracture, hard grades present a conchoidal fracture
(Test 5)	Lustre	Bright to dull
(Test 6)	Streak on porcelain	Brownish-black to black
(Test 7)	Specific gravity at 77° F.	0.90—1.07
(Test 9c)	Consistency at 77° F.	2—30
(Test 9d)	Susceptibility factor	8—40
(Test 10)	Ductility	Variable
(Test 11)	Tensile strength	Variable
(Test 15a)	Fusing point (K. & S. method)	80—300° F.
(Test 15b)	Fusing point (Ball and ring method)	100—325° F.
(Test 16)	Volatile matter, 500° F. in 4 hours	1—12%
(Test 17a)	Flash point	350—550° F.
(Test 18)	Burning point	400—650° F.
(Test 19)	Fixed carbon	5—20%
(Test 21a)	Solubility in carbon disulphide	95—100%
(Test 21b)	Non-mineral matter insoluble	0—5%
(Test 21c)	Mineral matter	0— $\frac{1}{2}$ %
(Test 22)	Carbenes	0—10%
(Test 23)	Solubility in 88° naphtha	50—90%
(Test 24)	Solubility in other solvents	Largely soluble in turpentine and benzol, and slightly soluble in alcohol and acetone
(Test 25)	Water	Absent
(Test 28)	Sulphur	Trace —7.5%
(Test 30)	Oxygen	2—5%
(Test 33)	Paraffin	0—10%
(Test 34)	Saturated hydrocarbons	30—75%
(Test 35)	Sulphonation residue	90—100%
(Test 37)	Saponifiable constituents	Trace —2%
(Test 40)	Glycerol	None
(Test 41)	Diazo reaction	No
(Test 42)	Anthraquinone reaction	No

Sulphurised Asphalts.

Under the action of heat, sulphur has a sort of condensing action on asphalt—analogueous to vulcanisation possibly. Abraham represents the process roughly as $C_nH_{2n} + S = C_nH_{2n-2} + H_2S$.

Numerous patents have been effected for sulphurising asphalts, fatty acid pitch, coal-tar pitch, grahamite, etc., but the use of these sulphurised bodies has generally been abandoned.

Recently, however, H. Burnice¹⁴¹ has treated residues from Roumanian crude oil with about 7.5% sulphur, and claims to have produced a particularly good product.

Sludge Asphalts.

These are not now produced to the extent that formerly obtained. They are characterised by the following features: intense black streak, high percentage of sulphur, high percentage of oxygen, which distinguishes them from all other forms of asphalt and the small amount of paraffin and saturated hydrocarbons they contain.

Much discussion and investigation have centred on the problem of satisfactory methods for differentiating the various natural and artificial asphalts and bitumens, and one may cite as references the publications of Hutin,¹⁴² Graefe,¹⁴³ Pailler,¹⁴⁴ Marcusson¹⁴⁵ and Richardson.¹⁴⁶ The conclusions drawn by the last-named investigator are particularly noteworthy, for it is shown that the natural Trinidad and Bermudez asphalts consist largely of unsaturated hydrocarbons, and following in order of increasing percentage of saturated hydrocarbons we have respectively Trinidad residual pitch, Mexican petroleum pitch, Californian petroleum pitch, and Texas petroleum pitch. From this follows the very important conclusion that the greater the percentage of saturated hydrocarbons in a bitumen the less pronounced are its asphaltic characters.

E. C. Pailler¹⁴⁷ has pointed out the differences between natural and petroleum residual asphalts based on estimation of the fixed carbon, the acidity of the liquid obtained on careful dry distillation and on the saponification value.

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CHAPTER XV

COAL-TAR PITCH AND ALLIED PITCHES

Residuals in Pyrogenous Distillation—Occurrence, Genesis and Composition of Coal—Destructive Distillation of Coal—Composition, Properties and Uses of Coal Tar—Coke Oven, Producer Gas and Blast Furnace Tars—Distillation and Properties of the Resultant Tar Pitches.

IN this country the best known pitch and that produced in by far the largest amount is the familiar Coal-tar Pitch, and under this heading will be considered the pitches corresponding to the tar recovered as by-products from bituminous coal carbonised or consumed in

- | | |
|----------------------------|--------------------|
| 1. Illuminating Gas Works. | 3. Blast Furnaces. |
| 2. Coke Ovens. | 4. Gas Producers. |

According to a recent return,¹⁴⁸ the quantities of Tar Pitch produced in Great Britain in the years 1922 and 1923 were as follow :

	1922.	1923.
From gas and coke-oven works	(tons) 490,573	624,641
From other works	(tons) 23,663	52,721

The consideration of the production of the tars themselves is rather outside the scope of the present volume, and the reader is referred to any of the well-known works on Gas Manufacture, etc., for full information. It is not out of place, however, to point out that tars constitute the volatile and oily decomposition products obtained in the pyrogenous treatment of bituminous and other organic substances, such as shale, peat, greases, etc., and the resulting distillates are usually of liquid consistency, dark brown to black in colour, and have an odour usually characteristic. The synopsis reproduced on p. 113, due to Abraham, indicates the raw materials used and the modes of treatment.

The temperature to be employed depends much on the materials to be decomposed, but high temperatures result in the formation in the tars (and hence in the resultant pitches) of higher amounts of free carbon, due to greater thermal decomposition ("cracking" or "pyrolysis"), and also lead to the formation of a very large number of hydrocarbons and allied substances in addition. This subject of the pyrogenesis of hydrocarbons has been treated fully by A. E. Dunstan, F. B. Thole and E. L. Lomax,¹⁴⁹ and the reader is referred to the survey by those authors of the chemical problems involved.

Coal-tar Pitch is a product of the distillation of coal tar, which in turn is a by-product in the manufacture of illuminating gas from coal, the yield of tar in such manufacture being approximately 4%

TABLE XXIV.
Residuals in Pyrogenous Distillation.

Raw materials used.	Heat alone ("Destructive distillation").	Partial decomposition.		"Cracking" of oil vapours.
		Air and steam ("Producers").	Limited access of air.	
Bituminous substances :				
Petroleum products .	—	—	—	{ Oil-gas tar Water-gas tar
Peat	Peat tar	Peat tar	—	
Lignite	Lignite tar	Lignite tar	—	—
Pyrobituminous shales	Shale tar	Shale tar	—	—
Bituminous coals .	{ Gas-works Coal tar Coke-oven Coal tar	{ Producer-gas coal tar	Blast-furnace tar	—
Other organic materials :				
Wood	Wood tar	—	—	—
Bones	Bone tar	—	—	—

of the weight of coal carbonised. As coal, therefore, is the ultimate parent of coal-tar pitch, it is of interest to know something of the former. Stopes and Wheeler ¹⁵⁰ have defined coal thus : " Ordinary coal is a compact stratified mass of mummified plants (which have in part suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter. Veins, partings, etc., which are found in nearly all coal are local impurities and are not part of the coal itself."

Coal is found in many parts of the world, by far the largest deposits (chiefly humic or so-called bituminous coal) occurring in the Coal Measures of the carboniferous period. The coal-forming vegetable materials have accumulated in a variety of ways—on land, in sea-water, in fresh-water, and in brackish water. Bone ¹⁵¹ has recently put forward in tentative outline a scheme indicating the possible formation of coal through various stages, commencing with the lignocelluloses, vegetable proteins and resins composing the original vegetable material.

Researches by leading geologists and botanists indicate that coal has been formed from plants occurring in the following groups :

Thallophyta (algæ and fungi).

Bryophyta (mosses and liverworts).

Pteridophyta (ferns, horsetails).

Gymnospermæ (the Araucariæ, Cycadaceæ, Ginkgoaceæ).

Coals vary much in character, and it is found convenient to divide them broadly into the following groups : ¹⁵²

1. Brown Coals or Lignites.
2. Sapropelic Coals $\left\{ \begin{array}{l} \text{Cannel Coals.} \\ \text{Bogheads or Torbanites.} \end{array} \right.$
3. Humic or Bituminous Coals.
4. Anthracite Coals.

As we are here concerned only with a product derived ultimately from bituminous coals, it is sufficient to confine our attention to coals of this class which are black, of more or less even brightness and which separate into more or less rectangular pieces when broken.

Various schemes for classification of coal on an analytical basis have been put forward, though none is satisfactory. But Lewes ¹⁵³ suggested that the coking or non-coking power of coal will depend upon the preponderance in the first case of resinous bodies and hydrocarbons, and in the second case of humus bodies and residuum (carbon).

The study of the action of solvents on coal has received much attention in recent years, and Clark and Wheeler ¹⁵⁴ have come to the conclusion that coal contained two main groups of bodies, "humous" and "resinous" respectively. Jones and Wheeler ¹⁵⁵ obtained a solid paraffin, chiefly heptacosane ($C_{27}H_{56}$), from a bituminous coal. An investigation on the resinic constituents and coking properties of coal has been carried out by W. A. Bone, A. R. Pearson, E. Sinkinson and W. E. Stockings, ¹⁵⁶ and a number of important results have been recorded.

It is evident that the coal substance can be divided into two main groups, viz., cellulosic (humic) and resinic, and hydrocarbon bodies (both saturated and unsaturated), and resinous bodies have been isolated, which indicates that these compounds exist in the free state in many types of coal.

A comprehensive review of the present knowledge of the composition, properties and uses of coal-tar pitch is given in a paper by Weiss, ¹⁵⁷ who points out that the character of the pitch depends on :

- (a) The character of the tar distilled.
- (b) The percentage of total distillate removed.

But, as is pointed out by Butler, ¹⁵⁸ the composition of coal tar is so varied, and is dependent on such a variety of factors, that no analysis that is fairly representative can be given. This investigator further adds that coal tar varies principally as follows :

(1) That containing a preponderance of open chain paraffinoid bodies and giving a lower yield of pitch.

(2) That characterised by the presence of closed chain aromatic compounds, free carbon and leading to a greater yield of pitch.

The specific gravity of coal tar varies in practice between 1.070 and 1.215, according to temperature of carbonisation and the type of retort used. According to Wright,^{158a} lower specific gravity tars generally result when a low-carbonisation temperature (800° C.) is used, or if the coal be carbonised in vertical retorts, whereas high temperatures (1100° C.) and the employment of horizontal retorts lead to high gravity tars. The point of this is that the lower specific gravity tars are more aliphatic in character, and thus influence the properties of the pitch subsequently produced; such tars arise in the relatively new Del Monte process of distilling coal.

The extent to which tars vary in their yield of commercial distillates is indicated in the following table, due to E. G. Stewart.¹⁵⁹

TABLE XXV.
Commercial Distillates from Gas Works Tar.

	Works using high heats and light charges.	Works using moderate heats and fairly heavy charges.	Continuous vertical retorts.
	%	%	%
Water	2.0	2.0	2.0
Light oils	1.0	6.0	5.6
Carbolic and creosote oils	14.0	32.0	41.4
Anthracene oil	5.0	4.0	4.0
Pitch	78.0	56.0	47.0
" Free carbon " in pitch .	36.0	17.0	5.5

Closely analogous to coal-tar pitch is coke-oven pitch from by-product coke ovens, used primarily for the production of coke. The coking is, of course, a process of destructive distillation, and the character of the tar, and ultimately of the pitch produced, depends somewhat on the type of coke oven used and the method of recovering the distillates.

Lewes¹⁵³ gives the analysis of what may be considered a typical coke-oven tar as follows :

Semet-Solvay Coke Oven Tar.

Specific gravity	1.170
Light oil, 80—170° C.	3.7%
Middle oil, 170—230° C.	9.8%
Creosote oil, 230—270° C.	12.0%
Anthracene oil, over 270° C.	4.3%
Pitch	67.0%
Water	2.3%

Blast-furnace coal-tar pitch is obtained from blast-furnace tar, in its turn a by-product of the blast furnace when the latter uses bituminous coal. Generally speaking, blast-furnace pitches are more paraffinoid than other forms of coal-tar pitch, and owing to their relatively high ash content (from the flue dust) are not so valuable.

By-products are recovered from the large producer-gas plants, of which several types are in use, and the tar is subsequently distilled for the production of the usual fractions.

The problem of coal-tar distillation concerns us here only in so far as it relates to the production of coal-tar pitch. Several types of still are commonly in use, various methods of heating are employed, and there are both continuous and discontinuous systems of tar distillation in use, not only in this country but abroad.

Amongst the commonest types of continuous-distillation plant in use in this country may be mentioned the systems due to Hird, Wilton and the Chambers and Hammond system.

Space forbids anything more than a brief outline of one of these systems, namely, the Hird continuous system, a typical installation of which is shown in the accompanying illustrations (Figs. 16–19), which, together with the following account of the working of the system, are taken from Warnes's book.¹⁵²

Briefly, the method in the Hird continuous system is as follows. The crude tar is conducted from the storage tank into the regulating tank; from this tank it flows to the steam preheater, then to the first of the series of heaters, a constant head being maintained by means of a float valve in the regulating tank. In passing through these heaters the temperature of the tar is raised by its receiving heat from the various distillates leaving the stills as they pass through the coils. During its passage the tar is deprived of practically all the contained water and the crude naphtha. The vapours of these materials pass into a common main, and thence through the tube of a coil condenser, in which they are condensed. The condensed liquids then pass through a sight box and a separator, and thence to their respective receivers.

After its passage through the heater-coolers the tar flows through the coil in the pitch cooler, and while doing this its temperature is further raised, whilst that of the pitch is correspondingly lowered. On leaving the pitch cooler the temperature of the tar may be

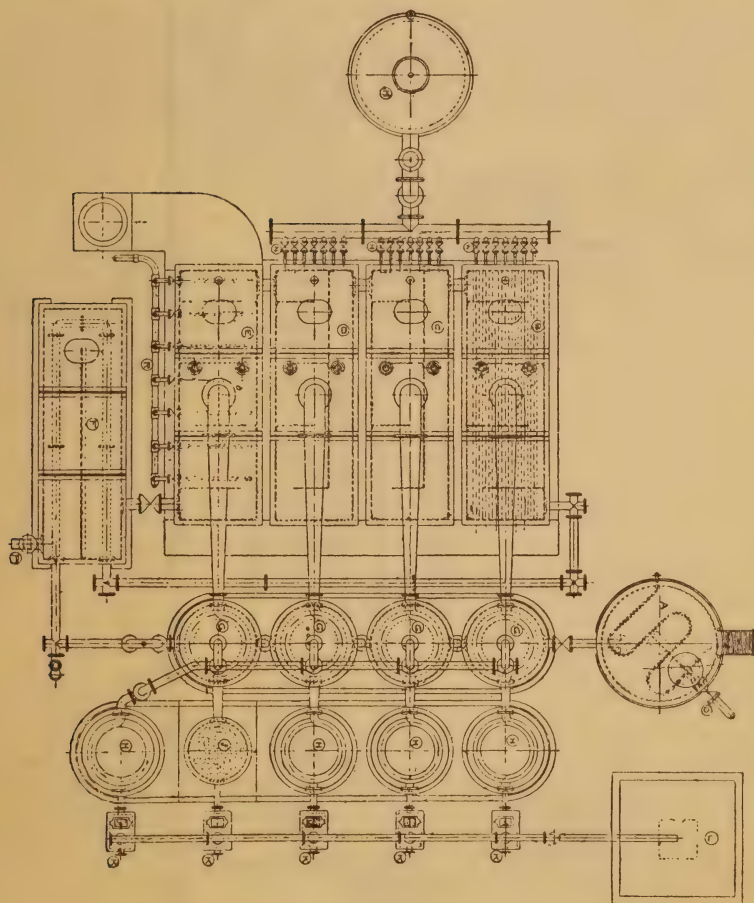


FIG. 16.—Plan of Hird's Continuous Distillation Plant.

from 120° to 200° C., according to the original composition of the tar. If the original water content has been high, much of the heat will have gone into the removal of water during the passage through the heaters.

The tar is now distilled for its light oil creosotes, etc., by adjusting the heating of the stills, so that as the tar flows through them in succession it shows such temperatures as have previously been

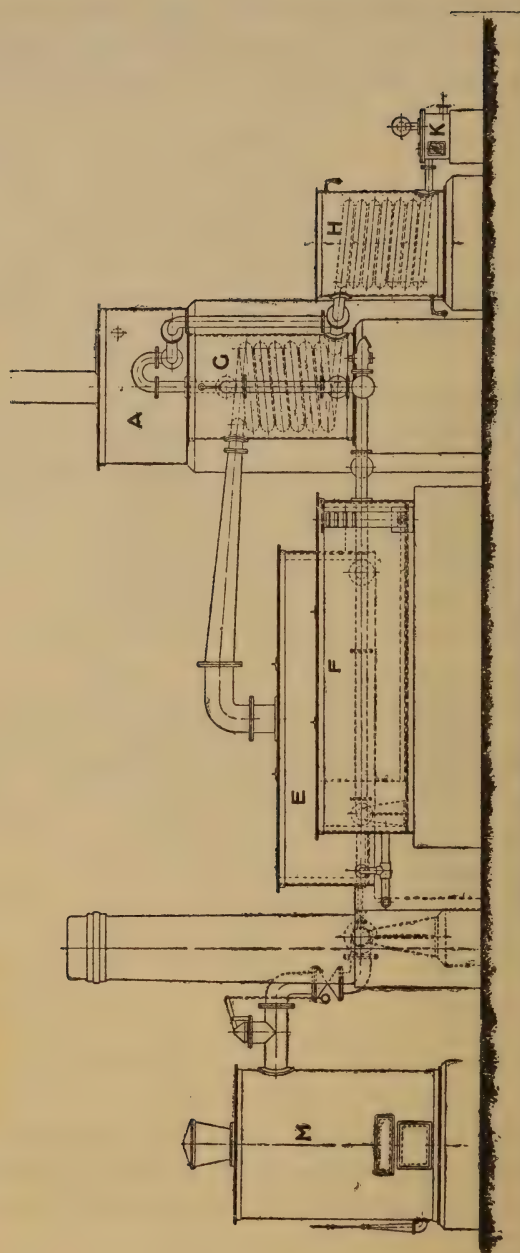


FIG. 17.—Hird's Continuous Coal-tar Distillation Plant.

found to give desirable oil fractions. The anthracene distillation is helped by live steam as usual in tar distilling.

The residue from the last still is liquid pitch, and this passes from the still into the pitch cooler, through which it travels on its way to the pitch bay, and during its progress it gives up much of its heat to the crude tar passing through a pipe immersed in it, on its way to No. 1 still. The temperature of the pitch on leaving the cooler is such that it practically inhibits the emission of irritating fumes so often observed when running off pitch in the intermittent systems of tar distillation.

With such a plant it is possible to adjust the temperatures so as to obtain continuously uniform fractions of any desired boiling point, whilst at the same time the pitch can be varied to meet any desired twisting point. Moreover, this plant may be worked with a coke-oven installation (Figs. 16, 17, 18 and 19).

Coal tar pitches show the following ranges according to Abraham :

TABLE XXVI.
Characteristics of Various Tar Pitches.

	Gas-works coal-tar pitch.	Coke-oven coal-tar pitch.	Blast furnace coal-tar pitch.	Producer- gas coal-tar pitch.
(Test 1) Colour in mass ...	Black	Black	Black	Black
(Test 2a) Homogeneity at 77° F.	Variable	Variable	Variable	Variable
(Test 2b) Homogeneity when melted ...	Uniform	Uniform	Uniform	Uniform
(Test 4) Fracture	Conchoidal	Conchoidal	Conchoidal	Conchoidal
(Test 7) Specific gravity at 77° F.	1.15—1.4	1.20—1.35	1.2—1.3	1.2—1.35
(Test 13) Odour on heating	Penetrating odour characteristic of all coal tar pitches			
(Test 15b) Fusing point (Cube method)	90—345° F.			
(Test 19) Fixed carbon ...	30—45%	20—45%	10—30%	20—45%
(Test 21a) Soluble in carbon disulphide	55—90%	60—85%	50—75%	60—85%
(Test 21b) Non-mineral mat- ter insoluble ...	10—45%	15—40%	15—35%	15—40%
(Test 21c) Mineral matter ...	0—1%	0—1%	10—20%	0—2%
(Test 35) Sulphonation residue	0—5%	0—5%	5—20%	0—5%

Carbon 90—95%, hydrogen 3—5%, sulphur 0.5—1%,
nitrogen 0.2—1.2%, oxygen trace to 2%.

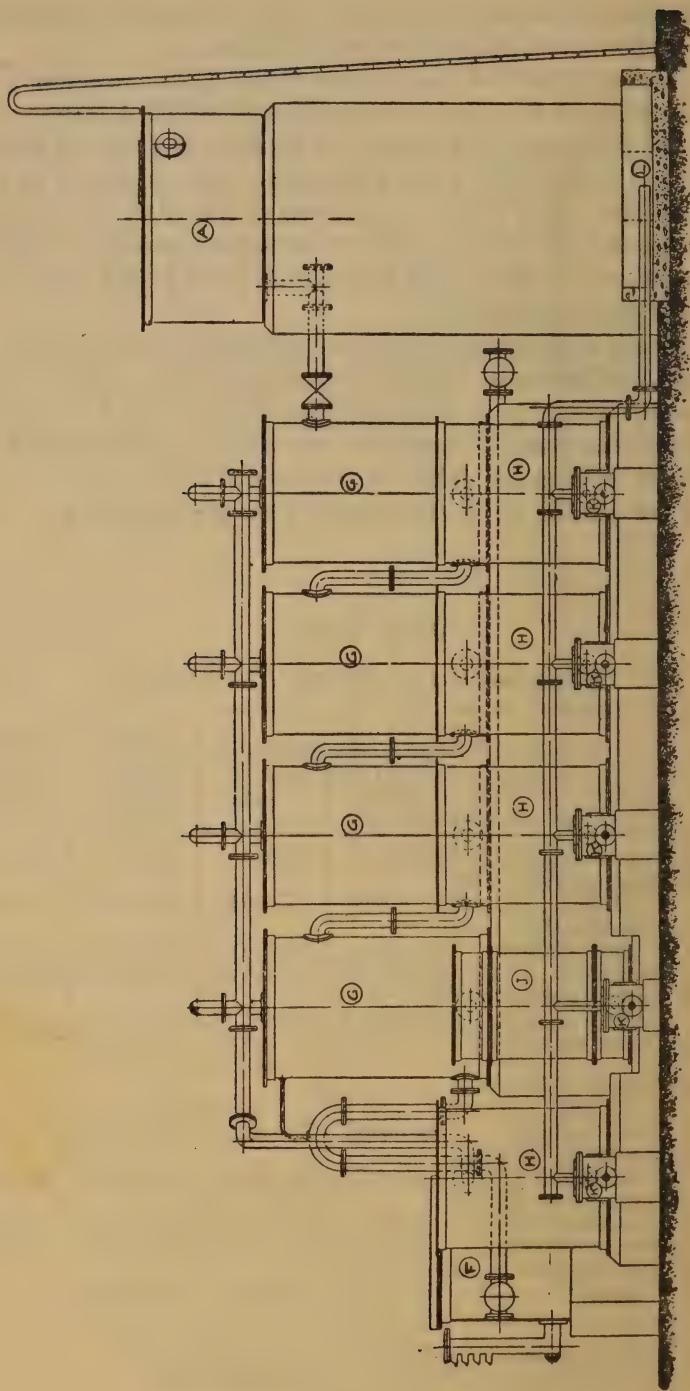


FIG. 18.—Hird's Continuous Coal-tar Distillation Plant.

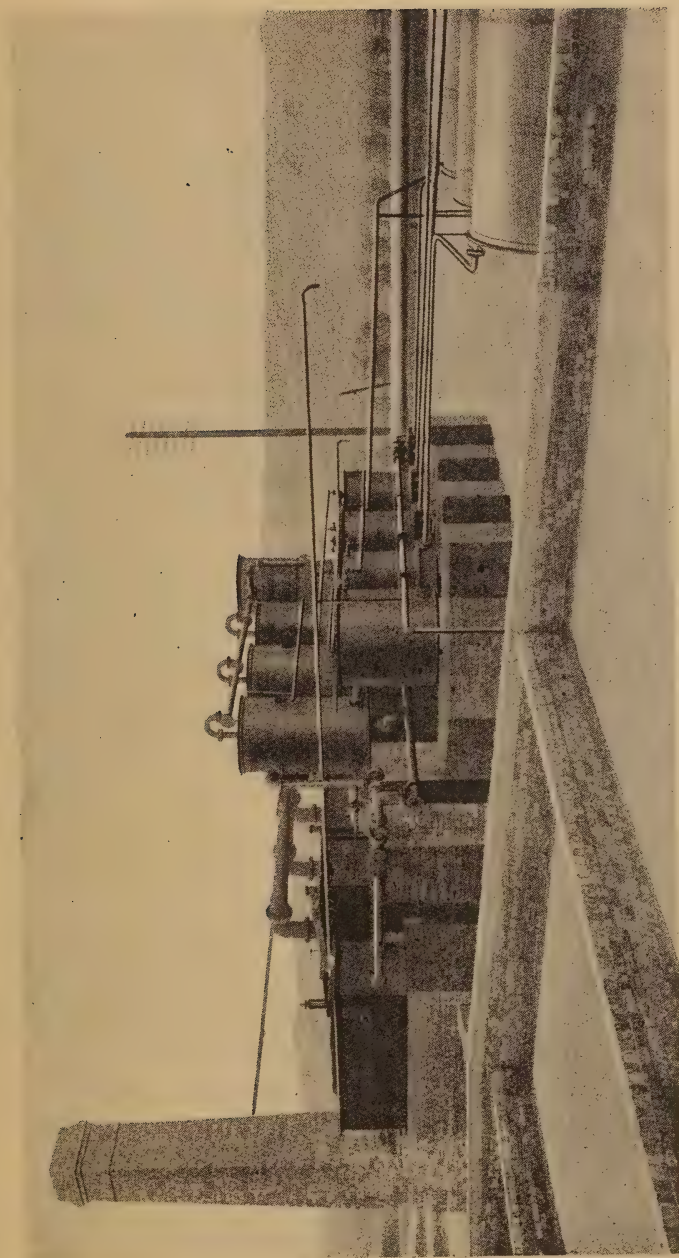


FIG. 19.—Hird's Continuous Coal-tar Distillation Plant.

All the pitches are largely soluble in carbon disulphide, benzol, coal-tar distillates, carbon tetrachloride and chloroform. They are only partially soluble in petroleum distillates and turpentine.

Concentrated nitric and sulphuric acids char and decompose coal-tar pitch, though if diluted the acids effect only slow disintegration, whilst hydrochloric acid (concentrated or dilute) and solutions of the caustic alkalies and ammonia have no effect. Air and water appear to be without action, but the softer pitches on exposure to the weather gradually harden, owing to the drying out of the oily constituents.

Coal-tar pitch is a complex mixture of hydrocarbons mainly belonging to the aromatic series, basic and non-basic nitrogen compounds and oxygenated compounds, all of high boiling point and "free carbon" (see Chap. X). According to Marcusson, coal-tar pitch consists of "free carbon," high molecular weight hydrocarbons, coal-like resins, soluble tar bitumens, phenols, cresols and, in addition, three distinct tar resins respectively soluble in benzol, carbon disulphide and pyridine; in addition, compounds of sulphur and nitrogen are present. The resins are said to be aromatic compounds of high molecular weight, and the one soluble in benzol will absorb oxygen, being thereby transformed into a mixture of the two other resins. On this property, so it is suggested, mainly depend the drying power and resinification capacity of coal-tar pitch.

According to H. Tindale,¹⁶⁰ coal-tar pitch can be separated into four constituents—oils boiling up to 300° C., "petrolenes," "asphaltenes" and "free carbon." In vertical retort tars, asphaltenes are said to occur in amounts of 25—30% and in horizontal retort tars to the extent of 35—40%.

The handling of solid pitch has presented problems consequent on its tendency to produce ulcerous and cancerous growths and inflammation of the eye,¹⁶¹ and this handling is now the subject of Home Office regulations. Incidentally, one may remark that, being brittle in cold weather, fatal explosions due to coal-tar pitch have been recorded, as the pitch dust is more highly inflammable than coal dust of the same degree of fineness.¹⁶²

According to T. Howard Butler,¹⁶³ one of the most successful modern methods of dealing with coal-tar pitch is to allow it while hot to run into pans holding approximately half a ton. When the pitch is cold the pans are picked up by a crane and swung into railway trucks.

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CHAPTER XVI

MISCELLANEOUS PITCHES

Wood-tar Pitch from Hard and Soft Woods—Wood Distillation—Rosin Pitch—Peat and its Distillation Products—Peat-tar and Lignite-tar Pitches—Water-Gas and Oil-Gas—Tar Pitches and their Properties.

Wood-tar Pitch.

THE treatment of wood by destructive distillation has already been touched upon in Chapter III, but in this chapter the volatile distillates will be discussed rather than the residual charcoal. During the period 1915—1918 wood distillation acquired considerable importance in this country. Several factories were erected and equipped with modern wood-distillation plant, only to fall into disuse and ultimately to be dismantled on the resumption of peace-time conditions.

According to a report of the U.S. Department of Commerce,¹⁶⁴ there were in 1923 in the United States 123 establishments engaged in wood distillation—77 utilising hard woods, 26 utilising soft woods, each with appropriate plant for recovery of the by-products, whilst the remaining 20 utilised different types of wood and did not recover the by-products.

In the forest regions of the Continent of Europe wood distillation is also of great importance, and it has been computed that prior to 1914 the yield of pure pine pitch from the distillation of resinous woods in the Russian forest area was about 124,000,000 lbs. annually, and this was largely exported from Archangel and constituted the Archangel or pine pitch of commerce.

Woods may be divided into two main classes, viz :

Hard woods—maple, birch, beech, oak, poplar, elm, willow, ash, chestnut. The distillation of these aims at the production of wood alcohol, acetate of lime, tar and charcoal.

Resinous or Soft Woods—pine, fir, larch, spruce, cedar. The distillation of these aims at the production of turpentine, wood oils, tar and charcoal.

The yield of pitch and its characteristics naturally are influenced by the type of wood distilled, and as a result of large-scale experiments on the destructive distillation of wood, J. C. Lawrence^{164a} finds that

(a) Rich, soft resinous woods, like the firs and pines, yield about 8·4% pitch.

(b) Lean soft woods yield 3·9% pitch.

(c) Hard woods, like oak, birch, elm, yield about 5·2% pitch.

Slightly different types of retorts and by-product recovery plants are used in distilling the two main types of wood, but in both cases the heavy oils or tars are fractionally distilled to yield pitch, hard wood yielding hardwood-tar pitch and the soft resinous woods yielding pine-tar pitch.

These two classes of pitch vary somewhat in their physical properties, owing to initial differences in the wood and to slightly different types of plant used, and in duration and temperature of the destructive distillation of the wood.

They comply mainly with the following characteristics, according to Abraham :⁸⁰

	Hardwood-tar pitch.	Pine-tar pitch.
(Test 1) Colour in mass	Black	Brownish black
(Test 2) Homogeneity	Uniform	Uniform
(Test 4) Fracture	Conchoidal	Conchoidal
(Test 7) Specific gravity at 77° F. ...	1.2—1.3	1.1—1.15
(Test 15a) Fusing point (K. & S.)	100—200° F.	100—200° F.
(Test 19) Fixed carbon	15—35%	10—25%
(Test 21a) Soluble in carbon disulphide.	30—95%	40—95%
(Test 21c) Mineral matter	0—1%	0—1%
(Test 37) Saponifiable constituents ...	5—25%	10—40%
(Test 37c) Resin acids	Up to 20%	Up to 40%

Wood-tar pitch consists largely of the methyl esters of the cresols, such as guaiacol and of the trihydric phenols, and on the latter probably depend its antiseptic and preservative properties. The pine pitches contain larger amounts of rosin acids than are found in the hardwood pitches. The contrasting properties of these two types of pitch are given by H. K. Benson and L. L. Davis.¹⁶⁵

A sample of English hardwood-tar pitch examined by the author⁸⁴ showed the following results—black colour, uniform, very brittle and with hackly fracture and a black streak :

Specific gravity at 15.5° C.	1.114
Melting point (cube method)	117° C.
Fixed carbon	16.2%
Mineral matter	0.092%
Soluble in carbon disulphide	63.7%
Odour on heating	very creosotic.

The sample was almost completely soluble in cold absolute alcohol.

Rosin Pitch.—This is somewhat similar in composition and properties to pine pitch. Oleo-resin, the sap of the long-leaf pine, is composed of turpentine and rosin, and by distillation is separated into these two main constituents. The rosin, in turn, is distilled

either with or without the use of superheated steam, or even *in vacuo*. If destructively distilled at atmospheric pressure, it yields about 16% of rosin pitch and various rosin oil fractions. According to V. Schweizer,¹⁶⁶ when rosin is distilled with superheated steam, the following yields are obtained :

Acid liquor	5.5—5.8%
Rosin spirits	11.25—12.0%
Blue rosin oil	49.0—50.5%
Brown rosin oil	10.25—10.65%
Rosin pitch	18.0—19.0%

Rosin pitch is usually hard and friable, contains considerable quantities of resin acids (10—45%), but is free from fatty acids and does not weather well.

Peat-tar Pitch.—Peat, a compressed mass from the decomposition of vegetable matter in a swampy environment, consists of a mixture of water, iron and calcium salts, vegetable fibres and humus acids and small amounts of nitrogenous and sulphur compounds. By many it is considered as the precursor of lignite in that chain of metamorphic changes which, commencing with the cellulose of woody fibre, leads ultimately to coals. The great obstacle to its commercial exploitation has always been the difficulty of satisfactorily dehydrating it and the process known as “wet carbonising” has offered the greatest possibilities. Now that the main difficulties inherent in its utilisation are said to be overcome by the proposals of W. Wieland,¹⁶⁷ its use should become more general.

Dry briquetted peat is distilled to a limited extent by a variety of methods, and yields gas, tar, ammonium compounds and a coke hard enough to be used in blast furnaces. The tar, a black, viscid liquid, is produced to the extent of about 9—10% of the air-dried peat, and on distillation dry peat tar yields the following, according to Abraham :

TABLE XXVII.
Distillation Products from Peat.

	Crude.	After Purification.
	%	%
Light naphtha	16	12
Heavy naphtha	30	25
Lubricating oil	15	13
Paraffin wax	12	2
Peat-tar pitch	16	16
Creosote	—	12
Loss	11	20

E. Börnstein and F. Bernstein¹⁶⁸ devised a process for the destructive distillation of crude peat, and the resulting tar, when dehydrated, yielded 47% of a paraffinoid pitch. According to G. T. Morgan and C. E. Scharff,¹⁶⁹ the redistillation of peat tar yields about 5.8% of a typical soft pitch with asphaltic properties.

Ordinarily peat-tar pitch has much the same properties as lignite-tar pitch, and has poor weathering properties.

Lignite-tar Pitch.—Brown coals (Lignites), cannel coals and bituminous shales all yield tars on destructive distillation, and these tars subsequently give rise to pitch, allied on the one hand somewhat to coal-tar pitch and on the other hand to wood-tar pitch.

Large deposits of lignite occur in the U.S.A., in Canada, to some extent in Australia, one small deposit at Lowe, in Derbyshire and in Germany. In the last-mentioned country low-temperature retorting¹⁷⁰ is resorted to in considerable extent.

Retort lignite is treated in one or two ways, thus :

1. Low-temperature destructive distillation.
2. Solvent extraction for the removal of montan wax and destructive distillation of the residue.

In the case of distillation, this takes place between 270° and 500° C., and the yield of tar is about 5—10% of the lignite distilled. The tar, which is of buttery consistency at the ordinary temperature, is dark brown to black in colour; and is composed of liquid and solid members of the paraffin and olefine series of hydrocarbons, together with small amounts of hydrocarbons of the benzol series and higher phenols and their derivatives (see Chapter X). There are also present about 10—25% of solid paraffin and 0.5—1.5% of sulphur. Asphaltic substances, however, according to Marcussou, are scarcely present.

The tar is fractionated into crude oil (33%), a paraffinoid distillate (60%), small amounts of other distillates and about 5% of lignite-tar pitch, or it may be continued to the stage of coke.

Lignite-tar pitch is characterised by the presence of phenols, the absence of insoluble carbonaceous matter, the presence of small amounts of paraffin wax, and almost complete solubility in benzol; these characters serve to distinguish it from coal-tar pitch. From wood-tar pitch it is distinguished by its content of sulphur and paraffin, and from asphalt and resin pitch by the diazo-reaction indicating the presence of phenols.

In the following table E. Graefe¹⁰⁸ has indicated the differences between lignite-tar pitch and many other residual pitches, thus :

TABLE XXVIII.

Comparison of some Residual Pitches.

	Average m. p. ° C.	Residue after benzol extraction	Sulphur.	Iodine value.
		%	%	
Lignite goudron	52	0.0	1.88	66.5
„ pitch	86	0.0	2.14	93.7
Coal-tar „	91—92	46.0	0.31	50.0
Wood-tar „	195	42.0	0.0	140.0
Petroleum pitch I	33	2.0	1.17	49.4
„ „ II	73	3.5	1.09	70.3
„ „ III.....	126	4.0	1.00	103.5

In Germany, by reason of its solubility in petroleum distillates, lignite-tar pitch finds extensive use in the manufacture of cheap paints.

The retorting of bituminous shales is also a source of shale tar and shale-tar pitch in many parts of the world, not only in the U.S.A., but in Australia, Germany and Scotland. Shale tar and the resulting pitch are more paraffinoid than asphaltic in character, and generally are closely similar in properties and composition to the corresponding products from lignite.

Water-gas and Oil-gas Tar Pitches.

These and their corresponding tars are allied on the one hand to petroleum asphalts, and on the other to coal-tar pitch. In modern water-gas plant, anthracite coal or coke undergoes partial combustion and is then subjected to the action of steam, leading to the production of “blue gas,” : $C + H_2O = CO + H_2$. This gaseous mixture is mingled with gas-oil and the resulting mixture passed through a superheater at 650—700° C., to crack the oil vapours. In this way a certain amount of tarry formation occurs, and below are given analyses of some of these tars.

TABLE XXIX.

*Water-gas Tars.*¹⁷¹

Sample.	1.	2.	3.	4.
	%	%	%	%
Water	1.5	1.0	—	—
Light oil	3.5	6.5	—	1.39
Middle oil	30.5	9.0	5.80	15.45
Heavy oil	20.0	18.5	9.16	—
Anthracene oil	25.5	42.0	34.34	42.39
Pitch	19.0	23.0	39.41	18.23

Oil-gas tars arise in the cracking or heating of petroleum alone in closed retorts, some 10% of tar being recovered in one of the processes employed.

Water-gas tar and oil-gas tar, when suitably dehydrated, are distilled by similar methods to those employed with coal-gas tar, yielding corresponding pitches, which resemble coal-tar pitch, from which they differ in containing paraffin to a certain extent and in their low content of "free carbon" (2—15%), *i.e.*, non-mineral matter, insoluble in carbon disulphide.

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CHAPTER XVII

FATTY ACID PITCHES

Subdivided into Stearine Pitch, Cotton-seed Pitch and Wool Pitch—Saponification of Fatty Oils—Cotton Black Grease and Wool Grease—Distillation Plant and its Operation—Characteristics of Various Stearine, Cotton and Wool Pitches—Bone-tar Pitch.

A GREAT variety of names has been used to designate the product Fatty-Acid Pitch, thus: "Fettpech" (German), "Kerzenteer" (German), goudron (French), candle pitch, cholesterol pitch, fat pitch, stearine pitch and many others.

It may be stated generally that all the fat pitches are residues remaining after the distillation of fatty matter in superheated steam, whether aided or unaided by diminished pressure.

The present author prefers the following subdivisions:

(a) Stearine Pitches resulting from the distillation of fatty acids produced by saponification of the familiar glyceride-containing fatty oils, such as tallow, palm oil, palm kernel oil, whale oil, etc.

(b) Cotton-seed Pitch, which is the residue after distillation of cotton black grease.

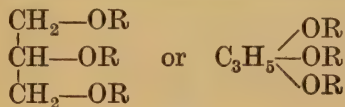
(c) Wool Pitch, which remains after distillation of wool grease or Yorkshire grease, this grease being chemically a wax, and not a glyceride.

The first important reference to stearine pitch is in a paper by E. Donath and R. Strasser,¹⁷² who mention that in the distillation of fatty acids used in candle manufacture, 2—7% of tarry matter remains in the still, and that on redistillation of this residue with superheated steam at 300° C. a black asphaltic mass of stearine pitch remains. It further appears that this pitch was used at Roubaix in the production of an oil gas.

(a) *Stearine Pitches*.—The raw material concerned in the manufacture of these pitches is the mixed higher fatty acids produced from fatty oils by saponification, and it is necessary to digress briefly here.

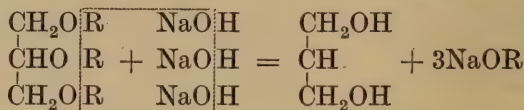
Our ordered knowledge of the subject of saponification was advanced when the constitution of fatty oils was established by the researches of Chevreul,¹⁷⁴ Berthelot,¹⁷⁵ and Wurtz,¹⁷⁶ when it was shown that these oils consist mainly of the triglycerides of the fatty acids.

The triglycerides may be represented by the general formula



where "R" represents any fatty acid radical, usually the radical of a higher fatty acid (see Chapter X).

Following the work of the early pioneers, the change which occurs when a fatty oil is boiled with a solution of a strong base such as caustic soda may be expressed by the formula



where R is the acid radical of any higher fatty acid, and for simplicity's sake the acid radical is supposed the same throughout.

The study of the hydrolysis or saponification of fatty oils has been carried on largely by Geitel,^{177, 178} Lewkowitsch,^{179, 180} Marcussou¹⁸¹ and others to the conclusion that this hydrolysis is stage-wise and may be indicated thus :

Triglyceride \longrightarrow diglyceride \longrightarrow monoglyceride \longrightarrow glycerol + fatty acids.

These reactions are interdependent, the rate of formation of the glycerol being conditioned by the rate of formation of the monoglyceride and so forth, the whole operation consisting of three simultaneous bimolecular reactions taking place in the same system, but not necessarily at the same rate, the older view of a quadrimolecular, direct action being regarded now as untenable. The present author has given elsewhere¹⁸² a full *résumé* of the investigations of this aspect of the subject. The demarcation into stages cannot be observed on a technical scale, partly because it is impossible to isolate or separately demonstrate the existence of the intermediate products of the stagewise hydrolysis.

Theoretical considerations show that water or steam is essential to saponification, but its use alone makes the completion of the reaction almost impossible on a technical scale, and in consequence various means have been introduced to hasten the reaction, and in modern industrial practice resolve themselves into :

1. *The acid process*, in which fats are boiled with concentrated sulphuric acid.

2. *The Twitchell process*, use being made of aromatic oleo-sulphonic acids.

3. *The autoclave process*, in which the fats are heated in contact with high-pressure steam in the presence of small amounts of alkaline-earths such as lime, magnesia, etc.

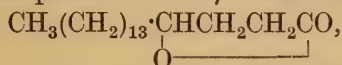
4. *The fermentation process*, which depends on the lipolytic action of certain enzymes, such, for instance, as that in the castor seed.

The technique of the foregoing processes need not be described here, but the reader is referred to the publications of Lewkowitsch¹⁸³ and to a *résumé* by the present author contained elsewhere.¹⁸²

Much of the early work on saponification concerned itself mainly with the chemical aspect of the subject, but in recent years the extension of our knowledge in relation to surface tension effects, colloidal phenomena, and the importance of emulsification and the part that these play in many familiar industrial operations, indicate that physical considerations may outweigh purely chemical ones when dealing with a heterogeneous system such as exists in the emulsion of fatty oil and aqueous alkaline or acid solution, which constitutes the reaction mixture in industrial saponification.

The function of the particular reagents, used technically in the various industrial methods of saponification already enumerated, becomes that of effecting intimate association of the reactants, and the accumulated evidence indicates that this association is best achieved by emulsification. The author has recently summarised the current views relative to the physical aspect of saponification.¹⁸⁴

In the acid process of saponification usually applied in the case of tallow and palm oil and similar fats, a change takes place in the reaction, leading to the production of γ -stearolactone,



and *i*-hydroxy-stearic acid, $\text{CH}_3(\text{CH}_2)_7\underset{\text{OH}}{\text{CH}}-\text{CH}_2(\text{CH}_2)_7\text{COOH}$, and

this is of importance in the subsequent distillation.¹⁸⁵

The distillation of the fatty acids is carried out by means of a plant of the type shown in Fig. 20. In this particular plant the still is of cast iron, 7 ft. in diameter and 7 ft. in depth from the top joint of the still, the body of which is cast in one piece, on to which is bolted a cast-iron cover, the whole being supported as shown. The contents of the still are heated by superheated steam by means of an internal steam coil. The principal fittings include a draw-off cock, feed valve, steam valve, safety valve and a self-recording thermometer, enabling the temperature of the still contents to be noted during the progress of the operations. The fatty acids are distilled in steam, and for this purpose an open steam coil through which passes superheated steam is passed into the still.

The cover is surmounted by a copper head with a copper vapour outlet connected to the condenser, which is a series of air-cooled vertical copper pipes, as indicated in the diagram. Each pair of tubes is provided with a bottom outlet separately connected to a copper worm condenser in a water-cooled worm tank, with suitable

outlets for the various distillates. The end of the condenser passes to a water-sealed fume-absorbing condenser or gas pan, of the cascade type, with water inlet valve and vapour vent pipe open to the atmosphere at the top. The still shown is arranged with a tubular feed heater, heated by means of the exhaust steam from the heating coil in the still.

Stills of similar design are in use for direct fire heat, the stills being then appropriately set in fire-brick with a suitably built flue, which carries the hot gases round the outside of the bottom of the still. Suitable setting of the still in the brickwork is of importance, so as to ensure the bottom of the still, rather than the higher parts of it, getting the bulk of the heating effect of the hot flue gases. When direct fire heat is used, it is necessary that a long cast-iron outlet pipe to carry away the pitch be cast solid with the body.

In an actual distillation the best practice is to work with steam of high superheat and a low pressure of about 5 to 8 lbs./sq. inch; the fatty acids distil over in the steam and are condensed in the series of air-cooled condenser pipes, and run away to collecting pails, arranged under the worm condenser, whilst the steam, together with any uncondensed lower fatty acids, and such products as carbon monoxide, carbon dioxide, acrolein and uncondensable hydrocarbons—the products of decomposition and pyrolysis in the still—pass away to the cascade condenser.

The aim of the distiller is to recover as much fatty acids from the still as possible, and thus reduce to a minimum the yield of pitch. The amount of recovery is determined somewhat by the nature of the material distilled, the extent to which the original fatty oil was saponified and the extent to which the distillation is carried. For fatty acids, testing up to 95–98% acidity (as oleic acid), the yield of pitch is lower than for fatty acids testing only 90% acidity. The longer the distillation is continued the less the yield of pitch and the less saponifiable matters such pitch will contain and the harder its consistency.

The author records hereunder the results of some actual large-scale distillations carried out under his control :

Autoclaved fatty acids from	Acidity (as oleic acid) of autoclaved material	Average yield of pitch.
	%	%
Tallow (English beef)	96.3	3.7
Palm oil (Niger)	94.5	3.8
Whale oil (No. 3)	94–96.2	8–9
Fish oil (Japan)	90–92	10–12

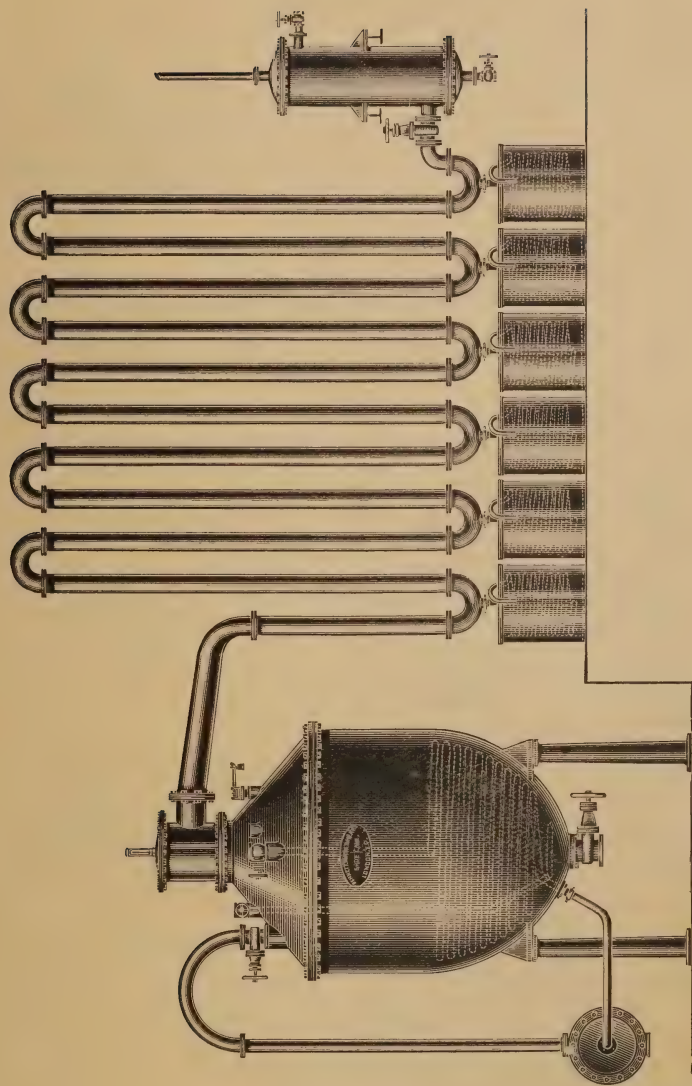


FIG. 20.—Fatty Acid Distillation Plant.

(By Bennett Sons and Shears, Ltd., 43, 44, Shoe Lane, London, E.C. 4.)

Characteristics of some stearine pitches from whale oil fatty acids examined by the author.⁸⁴

	Sample A.	Sample B.
(Test 1) Colour in mass	Black	Black
(Test 2) Homogeneity	Uniform	Uniform
(Test 4) Fracture	None—sticky	Brittle
(Test 5) Lustre	Bright	Bright
(Test 7) Specific gravity	1.016 @ 15.5° C.	1.046 @ 15.5° C.
(Test 15) Melting point (drop method)	37.9° C.	68.5° C.
(Test 21a) Solubility in CS ₂	97.1%	90.9%
(Test 21c) Mineral matter	0.48%	7.23%
Carbon	77.11%	73.19%
Hydrogen	10.35%	10.49%
Oxygen (by difference) .	12.06%	9.09%
Nitrogen	trace	} nil
Sulphur	nil	
(Test 37d) Saponification value ...	67.8	104
F.F.A. (as oleic acid) ...	10.7%	5.41%
(Test 44) Iodine value	126	97.9

Characteristics of some stearine pitches from palm oil fatty acids examined by the author : ⁸⁴

	Sample A.	Sample B.
(Test 1) Colour in mass	Black	Black
(Test 2) Homogeneity	Variable	Uniform
(Test 4) Fracture	None—pliable	Fairly brittle
(Test 5) Lustre	Dull	Bright
(Test 7) Specific gravity	0.982 @ 15.5° C.	1.060 @ 15.5° C.
(Test 15) Melting point (drop method)	43° C.	60.7° C.
(Test 21a) Solubility in CS ₂	94.62%	93.7%
(Test 21c) Mineral matter	2.98%	3.3%
Carbon	79.6%	76.80%
Hydrogen	11.26%	9.28%
Oxygen (by difference) .	6.16%	10.62%
Nitrogen	} nil	} nil
Sulphur		
(Test 37d) Saponification value ...	58.3	93.4
F.F.A. (as oleic acid) ...	8.7%	7.4%
(Test 44) Iodine value	118.5	94.3

(b) *Cotton-seed Pitch*.—Vegetable oils intended for edible purposes require to be refined in order to remove free fatty acids, suspended impurities and albuminous matter, colouring matter, and the resinous fatty unsaponifiable matter always found with the crude oil, and cotton oil is of particular interest in this connection. Crude cotton oil as obtained from the seed by crushing varies in colour from reddish-brown almost to black, the latter colour being that of Bombay cotton oil as ordinarily produced in English oil mills.

The first stage in the refining of this cotton oil is to heat it in large tanks tapering downwards to a cone piece at the bottom, the tanks being provided with suitable stirring gear and heating coils. Caustic soda solution of specific gravity about 1.125 is slowly run

through sprinkler pipes on to the heated agitated oil, with the result that combination takes place between the free fatty acids in the oil and the caustic soda, and ultimately soap separates out. On completion of the neutralisation and with cessation of the agitation the soap collects at the bottom of the tank, leaving clear bright neutral cotton oil at the top. The material which separates out is known as Cotton-seed Mucilage or Cotton Soap-Stock, and its composition is 30—40% cotton oil, 50—60% cotton fatty acids in the form of their soaps, traces of water, free caustic soda, albuminous matter and colouring matters.

Usually the cotton-seed mucilage is acidified with hot dilute sulphuric acid, and as a result a black grease, Cotton Black Grease, is thrown to the surface. This Cotton Black Grease, after settling, consists approximately of about 30% neutral cotton oil, 60% cotton fatty acids, albuminous matter, black colouring matter, fatty unsaponifiable matter and traces of water. It is sold to the distillers on the basis of 98% fatty matter soluble in carbon disulphide. Sometimes the separated black grease is saponified by one or other of the usual methods to which reference has already been made, in order to break up the neutral oil. A better method of achieving this end is to saponify the Cotton-seed Mucilage first before proceeding to the conversion into black grease.

Ultimately the cotton black grease is subjected to steam distillation, the same plant and procedure being adopted as that described in connection with fatty acids, with the result that light-coloured distilled cotton fatty acids pass over and a residue of Cotton Pitch or Cotton-seed Pitch or Cotton Stearine Pitch remains. The yield of pitch averages 10—20% of the weight of black grease distilled, representing 1—2% by weight of the original cotton-seed oil before neutralisation. The lower the percentage of neutral oil in the black grease, the smaller will be the yield of pitch, for on distillation the neutral oil does not always split to yield fatty acids which distil over in the steam, but a certain amount of breaking up into hydrocarbons and condensation products occurs, and these products remain in the pitch.

Cotton-seed pitch is usually produced in three grades: hard and brittle, rubbery, and soft, is usually black, uniform to variable in homogeneity, with a fracture varying from nil to conchoidal and testing generally within the following limits:

(Test 7) Specific gravity at 15.5° C.	0.90—1.20
(Test 15) Melting point (drop method)	Variable
(Test 21c) Mineral matter	2—5%
(Test 28) Sulphur	Maybe up to 1%
(Test 37a) Acidity (as oleic acid)	2—50%
(Test 37d) Saponification value (usually)	80—120

(c) *Wool Pitch*.—Wool grease is the oily material naturally occurring in sheep's wool and is extracted from the wool clip when this is suitably boiled with an alkaline soap solution and subsequently acidifying the liquor, whereby the grease is caused to rise to the top, and after removal, and appropriate purification and dehydration, it is obtained as a light to dark-brown grease of m. p. 30–40° C.

Chemically wool grease is an animal wax and consists of esters of the higher monohydric alcohols and higher monobasic fatty acids (see Chapter X), such as cetyl palmitate, $C_{15}H_{31}CO \cdot OC_{16}H_{33}$ (the ester of cetyl alcohol and palmitic acid), a certain amount of free higher fatty acids, and considerable amounts of unsaponifiable matter, the latter consisting of higher monohydric alcohols and cholesterol. Normally glycerides are not constituents of wool grease.

Wool grease is recovered in great quantity in the woollen centres of the West Riding of Yorkshire, where many of the Municipal Sewage Works have installed special plant for the recovery of the grease from the industrial effluent. This grease is subjected to steam distillation, without previous saponification, the same type of plant being utilised as for the distillation of fatty acids.

A number of typical samples of Yorkshire wool grease tested in the author's laboratory showed the following results :

TABLE XXX.

Analyses of Wool Greases.

	Inorganic matter.	Water.	Unsaponifiable matter.	Saponification value.	Acid. value.	Iodine value.
	%	%	%			
A ...	1.4	0.82	39.65	101.3	55.5	25.73
B ...	1.77	0.89	43.5	121.7	66.9	29.5
C ...	0.6	0.75	29.3	131.4	69.3	26.48
D ...	0.44	2.1	36.6	135	70.2	27.1

According to G. F. Pickering,¹⁰⁹ wool pitch has the following characteristics :

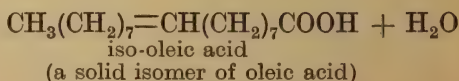
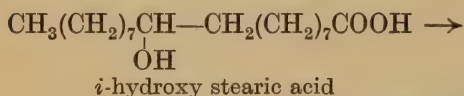
Soft to hard, dark brown to black, usually bright and of uniform consistency, specific gravity at 15.5° C., 0.97–1.0, melting point 90–160° F., ash 0.5–5.5%, saponifiable matter about 7% in hard pitches to 30% in softer samples.

Free fatty acids 0.75–15%, with 6% as an average, iodine value 35–45.

The various fatty-acid pitches (stearine, cotton and wool pitches) vary somewhat in their chemical and physical properties, due to differences in the materials from which they are made. According to the method employed in the preparation of the fatty acids, these bodies contain, in addition to the saturated and unsaturated fatty acids, small amounts of neutral fats, hydroxy-acids, anhydrides and lactones, fatty unsaponifiable matter and colouring matter. In the case of cotton black grease all the foregoing may be present, with the addition of albuminous matter and a larger percentage of neutral fats than found with the fatty acids. Wool grease, of course, contains no glycerides, but considerable amounts of higher alcohols and some cholesterol.

During distillation of these raw materials saturated fatty acids generally distil away first, but some of the unsaturated acids, such as oleic and those of higher unsaturation, are partly polymerised and partly suffer decomposition, being transformed into saturated and unsaturated hydrocarbons of the naphthene type (see Chapter X).

Some portion of the *i*-hydroxy stearic acid present in the fatty acids (when the acid process of saponification has been used) undergoes change thus to iso-oleic acid :



Condensations and intramolecular changes between some of the components in the still may also take place, and there is also a certain amount of cracking (pyrolysis), leading to the production of hydrocarbons, not only from the fatty acids and neutral fats, but (in the case of wool grease) also from the higher alcohols and cholesterol.

These pitches, therefore, may be regarded as complex mixtures of saturated and unsaturated fatty acids and condensed fatty acids, saturated and unsaturated hydrocarbons, some neutral fat, anhydrides and lactones, and in the case of wool pitch, cholesterol and the higher alcohols.

In view of the contrasting features of the several conflicting theories accounting for the genesis of petroleum and the asphalts, a detailed examination of the fatty acid pitches is of scientific interest and importance from the point of view of the possible formation of petroleum from animal matter and fish blubber.

All fatty acid pitches are converted into more or less infusible and insoluble and somewhat elastic masses on exposure to the atmosphere for long periods or even by heating to about 350° C. out of contact with the air. A sample of medium-soft pitch from whale oil fatty acids left exposed by the author ⁸⁴ for two months in a porcelain dish in the laboratory formed a tough, difficultly soluble skin on its surface. The iodine value, originally 123.8, diminished to 102.5 in the case of the surface skin formed. The weather-resistant properties of these pitches, due to the saponifiable matter they contain, makes them specially of value in the manufacture of certain japans and varnishes and in the production of certain waterproofing materials.

Bone-tar Pitch.—In the dry distillation of degreased bones (mentioned in Chapter III) a distillate, known as bone oil, bone tar, Dippel's oil, is produced as a by-product to the extent of 10–25% by weight of the bones. Fractional distillation of this tar yields Bone Pitch to the extent of about 23% of the tar. This pitch is somewhat intermediate in its properties between asphalts and fatty acid pitches. It is usually a hard, jet-black, very bright solid with a conchoidal fracture with m. p. about 100° C. It usually contains small amounts of sulphur, derived doubtless from the albumen in the bones from which it originates.

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CHAPTER XVIII

THE WEATHERING AND AGEING OF BITUMINOUS MATERIALS

Effects of Exposure to Air, Sunlight and Moisture—The Light Sensitiveness of Asphalt.

THE principal uses of bituminous materials, both natural and artificial, are in the manufacture of bituminous fabrics such as roofing felt, the waterproofing of damp courses, in electric insulation, in the manufacture of paints, varnishes, japans, in roadway and pavement construction and in a variety of other ways closely allied to the foregoing modes of employment. All these varied usages involve exposure in a greater or lesser degree to the action of moisture, sunlight and air, and comprised in what is termed weathering. This exposure involves changes, which may be negligible or important, in the physical and chemical condition of the bituminous substances.

M. Toch ¹⁸⁶ noted that some petroleum asphalts are unsuitable for making bituminous paints, and he has cited as an example a pure petroleum residual asphalt which, applied in a good continuous coat on cast-iron pipes in a cellar, lasted 3—4 years, whereas on the roof of a building exposed to direct sunlight the petroleum asphalt underwent complete decomposition in 20 days, with the liberation of "free carbon." His experiments indicated that this action was inhibited by incorporating an opaque pigment. Moreover, fatty oils (containing the triglycerides) are not affected in this manner and retard the disintegration of petroleum asphalts when blended with them.

Investigations of the weathering of bituminous substances have been conducted by P. Hubbard and C. S. Reeve, ¹⁸⁷ by S. R. Church and J. M. Weiss, ¹⁸⁸ by C. S. Reeve and B. A. Anderton ¹⁸⁹ and by C. S. Reeve and R. H. Lewis. ¹⁹⁰ The changes may be of a complicated character, being the cumulative effect of one or more of the following reactions.

Evaporation.—The more volatile constituents on exposure to air and the sun's rays are gradually lost. The tars particularly are liable to loss in this way, and the softer pitches harden owing to the evaporation of the more oily constituents, and usually the higher the temperature the greater the volatilisation.

Oxidation.—Exposure to the air brings this about more rapidly as a rule at high than at low temperature, and the action is two-fold, involving on the one hand direct union between oxygen and the bituminous substance, and on the other hand elimination of a

portion of the hydrogen in the form of water, and the conversion of the hydrocarbons in the bituminous substance to hydrocarbons of a lower degree of saturation, thus : $2C_xH_y + O_2 \rightarrow 2C_xH_{y-2} + 2H_2O$.

Carbonisation.—This really represents carrying to the stage of completion the oxidation of hydrogen and the consequent formation of “free carbon” in the bituminous substance; the reaction is most rapid in the presence of sunlight. Scrapings from a bituminous surface which has undergone such carbonisation are found to consist largely of fine particles of carbon.

Polymerisation.—This is due to a condensation or polymerisation of the molecules, and is shown by a hardening or setting of the bituminous substance. This takes place to a greater or lesser extent on heating bituminous substances; particularly is this the case with fatty acid pitches, and the more glycerides and the less fatty acids they contain, the more does this setting to a hard infusible mass take place.

Effects of Moisture.—The action of moisture may be two-fold—actual absorption of water and a gradual washing out of soluble constituents. Generally, though, this factor—the action of moisture—is less far-reaching than the previously enumerated factors.

Many of the harder naturally occurring asphalts suffer no change due to ageing or weathering, but we have seen that in the case of Trinidad lake asphalt a rapid hardening at the surface of the lake takes place. A hardening takes place also at the exposed surface of many petroleum residual asphalts, and in the case of many residual pitches. In an extended experience of fatty acid pitches derived from a variety of raw materials the author has observed how these on exposure become dulled and hardened at the surface, due to the action of light and air, and actual analyses revealed in these cases a decrease in the iodine value and an increase in the oxygen content of the fatty pitch.

According to P. E. Spielmann,⁸³ the change occurring in the case of many residual bitumens is twofold and involves a slow surface hardening, due to the action of light and air on the residual oils remaining in the bitumen, and a slower “settling down.” He makes the tentative suggestion that this latter phenomenon is due to “internal molecular rearrangement,” and in support of this view quotes the determinations given in the table at top of p. 140, which were obtained on a sample of residual bitumen.

The increases in asphaltene content and in fusing point are considered to support the theory of “internal molecular rearrangement.”

Penetration of Ageing Residual Bitumen.

Time in days.	At surface.	3 mm. below surface.	Asphaltenes.	Fusion point ° C.
0	46	—	31.5%	56.0
7	42	45	—	—
43	38 (35—41)	43 (41—44)	—	—
205	25 (20—30)	39 (36—42)	—	—
487	23 (21—26)	33 (30—40)	38.9%	58.3

Spielmann^{83a} also advances the view that the immediate surface hardening—besides being due to oxidation, the action of light and polymerisation—may be correlated with the presence of paraffin wax or ceresine in the bitumen.

Summarising, it appears that weathering and ageing affect bituminous substances by making their colour lighter, destroying their homogeneity by the formation of free carbon and dulling the surface. There is usually an increase in the specific gravity, hardness, viscosity, melting point, flash point, and decreases in the case of the amount of volatile matter, solubility in carbon disulphide and 88° petroleum naphtha. The amount of saponifiable constituents remains unchanged. Such physical properties as ductility, tensile strength and adhesiveness also undergo diminution.

The sensitiveness of bituminous materials to light, regarding the matter largely from a physical aspect, may be considered in this chapter. This light-sensitiveness of bitumen has been known since the time of J. N. Niepce, who in 1824 produced a portrait as a result of experiments with a solution of "asphalt," and the property has been made use of in a number of photo-mechanical processes. More recently the study of the subject has been revived. Maderna,¹⁹² for example, has found that different portions of a bituminous complex possess a light-sensitiveness differing in magnitude, though in each case of the same quality, and Paul Gödrich¹⁹³ found that petroleum asphalts free from paraffins are, relatively to other asphalts, the most sensitive towards light.

J. Errera¹⁹⁴ has made a careful study of the light sensitiveness of Judean asphalt and in this connection classifies its constituents into α -, β -, γ -resins, the last-named being sensitive to light and existing in the colloidal condition, the asphalt as a whole being both molecularly and colloiddally dispersed. Whatever be the underlying cause of this light sensitiveness, it appears to be established that it is intimately associated with colloidal phenomena.

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CHAPTER XIX

BITUMINOUS FABRICS

Roofing Felt—Floorings and Floor Coverings—Bituminous Cements, Insulating Coverings and Papers—Waterproofing and Damp Coursing—Manufacture and Uses of Bituminous Fabrics.

BITUMINISED fabrics are utilised in roofing, flooring, waterproofing, and for sheathing and insulating purposes, and they will be considered in detail under these headings.

Sheet Roofings.—These are composed of a single layer or a plurality of layers together, each layer being composed of a woven or felted fabric, which is saturated and/or coated with suitable bituminous materials, the bituminous materials being chosen largely on their ability to withstand weathering.¹⁹⁵

Both felted and woven fabrics are chosen, but the former are preferable, as they absorb a larger amount of bituminous material, and to a more uniform degree than is found possible with the latter type of fabric. Roofing felt is composed of a variety of fibres, the following, together with their approximate relative durability, expressed numerically, being, according to Abraham :⁸⁰

Wool	100
Cotton	60
Jute and manilla	44
Paper (including mechanical and chemical wood fibres) .	20

Wool fibres, besides being the most durable, are least affected by exposure to moisture and the sun's rays : incidentally they are the most expensive. Numerous substitutes for felting have been suggested, such as leather, cane, straw, coconut, moss, peat, sea grass, and numerous patents relative thereto have been taken out, but in most cases the above substitute fibres result in increasing the brittleness or porosity of a felt with which they are incorporated. In regard to woven fabrics, the most usual are hessian (of jute fibres), and duck (of cotton fibres).

The details of manufacture of the fabrics, and the technique of their saturation or coating with appropriate bituminous material, and the type of machinery employed are outside the scope of our survey. The materials generally to be recommended for the impregnating of the fibres and fabrics should be of soft consistency at ordinary temperature, with a penetration of more than 60 at 25° C. (Test 9b), a consistometer hardness (Test 9c) of less than 15 at 25° C., and a fusing point of 80—140° F.

The following classes of bituminous materials have been recommended in this connection for saturation :

Group I. Pure native asphalts, petroleum residual asphalts,

blown petroleum asphalts, and the pitches from wood tar, rosin, bone tar and fatty acids, either singly or blended to give the right consistency. If they are too hard they may be blended suitably with the softer grades of the pitches already enumerated, as well as with animal or vegetable fatty oils and wool grease.

Group II. Oil-gas-tar pitch, water-gas-tar pitch, coal-tar pitch, coke-oven pitch, wood-tar pitch and rosin, bone-tar and fatty acid pitches, alone or in combination, or, if necessary to effect the desired consistency, with the corresponding liquid tar, previously evaporated to expel the highly volatile oils, etc.

The tar and pitch compositions in Group II (except the fatty acid pitch) are used mainly for manufacturing multiple-layered prepared roofings, and for single-layer tarred felt, which is to be used in built-up roofings of more than one course of fabric. Only Group I compositions are recommended for general use, on account of their greater weather-resisting characters.

The characteristics of tar and pitch composition should correspond with those for a soft coal-tar pitch, *i.e.*, one having a fusing point 120—160° F. (cube method). Saturating mixtures prepared from asphaltic products should comply with the following characteristics, according to particulars given by Abraham :

(1) Viscosity at the saturating temperature should be as low as possible to accelerate the speed of absorption by the fabric.

(2) Penetration at 25° C. should be in excess of 60, and consistency less than 15, to prevent brittleness in the fabric.

(3) The susceptibility factor should be as low as possible, and preferably below 30.

(4) The saturant should be ductile.

(5) Fusing point 110—150° F., and as low a content of volatile matter as possible—less than 3% after 4 hours at 500° F.

(6) Preferably 97% or more of constituents soluble in carbon disulphide.

(7) Should be weatherproof.

The most commonly used materials for saturation purposes are soft coal-tar pitch, soft residual asphalt, and soft blown petroleum asphalt. A recent U. S. Government ¹⁹⁶ specification for coal-tar pitch for roofing purposes requires that the pitch when freshly melted should be glossy black, and not dulled in one week; m. p. 60—65.5° C., specific gravity 1.22—1.34, ductility—minimum 50 cm.;

free carbon content 15—30%. In the distillation test not more than 12% by weight should distil over below 300° C., and the distillate should show a specific gravity not less than 1.03.

Asphalt for use with asphalt saturated rag felt for roofing and water-proofing, and in the construction of mineral-surfaced roofing on an incline of not more than 3 in. to the foot, may be either petroleum residual asphalt or a mixture of refined Trinidad asphalt with petroleum asphalt, according to the latest U.S. Government specification,¹⁹⁷ which requires that the material when freshly melted shall be uniformly glossy and on ageing for one week its surface shall not become dull or show any separation of oil, grease, or wax. The asphalt shall further have :

M. p. (ball and ring method) 60—73° C.

Penetration 25—50 at 25° C., with a minimum of 10 at 0° C.

Ductility at 25° C. to be 5 cm., preferably not less than 20.

Soluble in carbon disulphide (in case of petroleum asphalt only) minimum 99%.

Ash (in case of mixture containing Trinidad asphalt), minimum 20%.

The ash must show the characteristics of that from Trinidad asphalt.

Naturally a great variety of modifications of the foregoing methods of using bituminous materials in the construction of roofing fabrics are to be found, and many might be enumerated. For instance, an impregnating material resembling rubber and suitable for coating millboards and textile fabrics has been patented by O. Schreiber.¹⁹⁸ Stearine pitch, wool pitch, or even coal-tar pitch or petroleum pitch is heated, cold air forced through, and during this treatment suitable oxidising materials are added. A somewhat similar material from the point of view of its applicability can be obtained by treating wool pitch with sulphur at temperatures up to 300° C.¹⁹⁹

Floorings.—Bituminous materials find considerable use in the construction of floorings laid down in somewhat the manner of a concrete floor, over which they have the advantage of a certain resiliency. Both natural and artificial asphalts, with or without suitable fluxing, are used, and mineral aggregates in the nature of crushed limestone, finely-graded sand are added, and finely-powdered pigments and coloured metallic oxides, such as red oxide of iron, chromium oxide, etc., may be added to give a decorative effect.²⁰⁰

This type of floor covering is laid down whilst of plastic trowelling consistency, the bituminous material being melted before admixture,

and the matrix on cooling hardens to a smooth, hard surface which wears better than a concrete surface.

As coverings for floors, but used in a somewhat different manner, there has grown up during the last fifteen years the manufacture of substitutes for linoleums and the like, bituminous materials, notably fatty acid pitches, being employed, the technique of which is somewhat analogous to that of linoleum manufacture (cf. "The Chemistry of Drying Oils," by L. S. Morrell and H. R. Wood). The finished product is prepared in rolls and laid down in squares and strips. The use of stearine pitch in this connection was patented during the World War,²⁰¹ and very considerable quantities of medium soft stearine pitch found application in the manufacture of floor coverings, where its plasticity, high viscosity and ready hardening on exposure render it valuable.

Bituminous Cements.—These are of plastic consistency and can be utilised in the manner adopted for handling lime-mortar and cement, and their use is for joining, filling in and repairing of damp-proof masonry. They consist of :

1. Bituminous base with or without the addition of vegetable oils, resins, etc.
2. Mineral matter such as finely-ground limestone, barytes, etc., as filler.
3. Fibrous matter such as shoddy, asbestos, slagwool, cotton flocks, to bind together the bituminous base.
4. Volatile solvents such as petroleum products, wood and tar distillates, in which the base will dissolve.

The bituminous materials should be blended to give a fusing point (K. & S.) of 135—175° F., a consistometer hardness (Test 9*b*) of 5—25 at 25° C., a susceptibility factor (Test 9*d*) below 25, and almost complete solubility in the solvent used. Further, the bituminous base or bases are melted together in the usual type of varnish kettle over direct heat, cooled until the mass begins to thicken and then the solvent is added. Alternatively, the ingredients of the base may be acted upon by the solvent in a closed, steam-heated and mechanically agitated tank. After the incorporation of the base and solvent, the other ingredients are added until the requisite pasty consistency is achieved.

Numerous acid-proof cements and acid-proof layers for floors are in use containing coal-tar pitch and other pitches in admixture with cement, fireclay, graphite, asbestos fibre, and other suitable materials.²⁰² The cements are particularly useful in the making of

joints in chemical plant, earthenware pipes, etc., and the bituminous material serves partly to bind together the various ingredients of the cement, and further, in virtue of its resistance to air and water, corrosive acids and chemicals generally, is invaluable in chemical and allied works, where steam and acid and other chemical fumes are encountered.

Water-proofing and Damp-proofing.

Their impermeability and resistance to the effects of moisture, make many bituminous materials and pitches invaluable in the prevention of the passage of moisture through porous constructional materials. By damp-proofing, according to G. J. Ward,²⁰³ is implied the prevention of the passage of water through brick, concrete or stone by capillary action; water-proofing or damp-coursing is the prevention of the passage of water under pressure through the walls of tunnels, conduits, tanks, etc., and calls for more than the comparatively thin layer of material which suffices to exclude moisture in damp-proofing work.

According to Ward, a damp-proofing compound must have several characteristics to fit in for its work. It must, first of all, yield a film which will be impervious to water, and must be durable even under decided temperature changes. It must be capable of easy and rapid application, and must dry fairly rapidly, so that, if necessary, more than one coat may be applied without any great loss of time. It must bind well to the surface on which it is applied, and must be inexpensive.

A great variety of damp-proofing compounds has been tried, but bituminous varnishes have generally proved so satisfactory in this respect that they are now consumed in very large quantities.

A bituminous varnish, to function satisfactorily in damp-proofing work, must have certain definite properties.²⁰³ In the first place, the varnish must be of a durable nature, maintaining its elasticity indefinitely. The percentage volatile at 100° C. is kept low as compared with the bituminous varnishes commonly applied to structural steel. This permits the attainment of a heavy consistency, which is desirable in order that in application a fairly thick coating is obtained. A thin coating applied to a porous surface, such as concrete, is drawn for some distance into the pores of the material, and fails to make a seal unless a number of coats are applied. The varnish must set within 8 hours, but may remain somewhat tacky for a period of several weeks. Finally, it must possess adhesiveness, bonding well to the surface on which it is applied, and

must be capable of acting as a foundation for plaster. The fact that these materials may be plastered on directly is one of the important considerations in their use. Experience shows, however, that the presence of certain materials or combinations enhances the effectiveness of the coating in its work. For instance, the presence of a percentage of stearine or fatty-acid pitch may be found to impart a desirable adhesiveness to the coating in addition to the great merit this material possesses of stability and retention, unimpaired, of its weathering and ageing properties after long exposure.

The only satisfactory criterion of the value of a bituminous varnish for damp-proofing work is an actual test conducted in a manner which parallels actual practice as nearly as possible. Two coats should be applied to the clean, dry, slightly rough surface selected, allowing sufficient time for setting between coats. It is necessary to obtain perfect continuity of the coating, any bare or thin places rendering the results worthless. The final coat of damp-proofing varnish is left slightly rough, and a coat of plaster applied. This is subsequently painted with a light-tinted flat paint. A satisfactory damp-proofing varnish prevents any appearance of moisture on the plastered wall, even when the outside of the wall is subjected to the action of water for lengthy periods.

Coal-tar pitch for use in this way, where the pitch is not exposed to a temperature in excess of 35° C., except during its installation, and where it is not subjected to vibration, should have the following characters : ²⁰⁴ Freshly-melted, the material must have a uniform black, glossy colour, and after ageing for one week must not become dull or show any separation of oily constituents. The freshly-fractured material must present a satin-black surface, m. p. (cube in water method) 52—60° C., free carbon 15—30%, *d* 1.22—1.34, minimum ductility 50 cm., and not more than 12% by weight, shall distil below 300° C., and the density of the distillate must not be below 1.03.

Natural asphalt is, of course, similarly used for water-proofing and damp-proofing, and a recent U.S. Government specification ²⁰⁵ requires asphalt for such use to be black and glossy when freshly melted; moreover, it must not become dulled in one week, it must have m. p. 60—77° C., penetration at 25° C. 25—50, at 0° C. a minimum of 10, and a maximum of 100 at 46° C. The ductility should be not less than a minimum of 15 cm. The maximum amount of volatile matter allowed is 1% at 63° C., whilst not less than 99% of the asphalt must be soluble in carbon disulphide.

Insulating and Sheathing Papers.

Paper is specially treated to enable it to take a water-proofing material, either by coating, by saturation, or by both methods of application, and such suitably water-proofed papers find great application in the construction of cold-storage floors, insulated rooms and spaces on ships, refrigerator cars for the transport of perishable foodstuffs of all sorts, and in the lining of ice chests, the object being to prevent the transfer of heat into enclosures, which it is required should be kept cold, and conversely to prevent the egress of heat from enclosed spaces requiring to be kept warm.²⁰⁶

Strong paper of open texture is the best to use in the manufacture of insulating papers, and generally the greater the number of layers used, the greater is the effectiveness of the insulated installation. In practice, the paper is introduced in the floors, walls and partitions of buildings between protective layers of wooden boards, one on each side of the cavity containing the chief insulating material, usually charcoal, cork or silicate cotton.

For water-proofing the papers, petroleum residual pitches of asphaltic character and fatty-acid pitches find the most frequent use. M. Dupré and S. Icard²⁰⁷ have patented the use of stearine pitch for water-proofing paper and fabrics, either by direct application or after solution of the pitch in a volatile solvent, and such substances as tar or resin may be added to assist the formation of a coating material. These coatings are odourless, impermeable, very elastic, and when used in the form of pitch papers are excellent damp-proof coatings for the walls of cold-storage rooms.

Cotton muslin strips $\frac{1}{2}$ —1 in. in width and 0.015—0.025 in. in thickness, passed through melted bituminous materials to fill up the pores of the fabric, form excellent coverings for electric cables, owing to the very high specific resistance of most bituminous materials and pitches. Pure native asphalts, petroleum residuals, blown asphalts, fatty-acid pitches, either alone or with asphalts, are used, and they should be tacky and adhesive at room temperature, and should retain this property as long as possible on exposure to the air.

The desiderata for bituminous materials for such work are a consistency at 25° C. of less than 7, a susceptibility as low as possible, fusion temperature 27—40° C., and after being maintained at a temperature of 500° F. for 4 hours, the loss of volatile matter should not exceed 5%.

Solid Impregnating Compounds.

Such compounds with a bituminous material as a basis are prepared for field coils and stationary windings. The impregnation is completed in one operation, the coatings are more chemically inert, are better fillers and more resistant to moisture. The temperature of impregnation for a "compound" is higher than for an insulating varnish, but it should not be above 175° C., or the cotton covering may be carbonised. These impregnating compounds, unlike insulating varnishes, require no thinners and solidify on cooling, rendering the enclosed parts insensible to vibration.

If an electrical machine be overloaded, the impregnating compounds will, unlike the varnishes, soften and may even melt; and if there be revolving parts, these may become exposed, owing to centrifugal force. Generally, the natural or petroleum residual asphalts and other materials used soften at 105—115° C., and do not become appreciably fluid below 150° C. The materials used—*asphalt, stearine pitch, rosin and copal*—are run together until water has been expelled, and, in order to make them resistant to mineral-oil, a certain amount of sulphur is incorporated. R. S. Morrell²⁰⁸ quotes the following as being typical of impregnating compounds:

1.	2.	3.
100 parts neutral wool fat	110 parts asphalt	Stearine pitch heated to 220—285° C.
200 „ asphalt	200 „ crude ozokerite	
50 „ rosin	70 „ rosin	
25 „ rosin oil		
(Andés)	(Seeligman and Zieke, p. 426.)	(Andés)

Being durable and elastic, and not cracking or running when exposed to extremes of cold or heat respectively, the petroleum pitches (preferably those of asphaltic character), by reason of their high insulating properties, are valuable even alone in the manufacture of electric cable insulations. But, as F. Dupré²⁰⁹ has shown, only first-grade bituminous materials, whether natural or artificial, are suitable for cable masses, viz., those with the requisite elasticity, ductility and adhesiveness, and a fusing point of at least 75—95° C. If use be made of those with a fusing point of only 40—60° C., then the cable mass will lose its form when exposed to external temperatures exceeding 20—30° C.

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CHAPTER XX

BITUMINOUS PAINTS, VARNISHES, ENAMELS AND JAPANS

Nature of Bituminous Bases Used—Volatile Solvents to be Used—Bituminous Paints and Varnishes Protective against Rusting and Exposure to Chemical Agents—The Jellying of Asphalt Paints—Japans and their Uses—Pitting of Japans.

PAINTS, varnishes, enamels, black japans, Brunswick blacks, stoving blacks are all prepared in the liquid state, and their consistency is regulated by the amount and nature of the solvent incorporated in the mixture. In this chapter attention will be confined to such of the above manufactured products as contain a bituminous base or material as an essential part of their composition, and, furthermore, they will be considered from the point of view of their composition, properties and uses. The technique of their manufacture closely simulates that of the manufacture of paints, varnishes, etc., in general, and the reader is referred to any of the well-known volumes dealing with paint and varnish manufacture for details of plant and *modus operandi*.

Bituminous Paints.—These consist of a bituminous base, a volatile solvent with or without the addition of vegetable drying oils, resins, fillers, pigments, etc., intended to dry or set by the spontaneous evaporation of the solvent, leaving a firm coat on the object painted. Generally those bituminous materials are chosen which will weather well on exposure to air, moisture and sunlight, and which are unattacked by mineral acids, caustic alkalies, cyanides and chemical fumes generally. One precaution that is necessary is to avoid the use of a bituminous base in any environment which will bring it into contact with the solvent action of any distillate (either in liquid or vapour form) derived from the same source as the bitumen itself, *e.g.*, coal-tar pitch should not be used as a paint or coating for materials which come into intimate contact with a coal-tar distillate such as coal-tar naphtha.

The bituminous paints may be divided into four groups containing :

- (1) Native asphalts, asphaltites, residual petroleum asphalts and all the pitches, with or without a filler, and suitable volatile solvents.

- (2) Bituminous substances, resinous substances (damar, sandarac, rosin), with or without a filler, or a coloured pigment, and suitable volatile solvents.

- (3) In addition to bituminous substances, animal or vegetable fats and oils such as linseed, tung, soya, fish, cotton, and perilla

oils, raw or thickened, and in conjunction with driers, and suitable volatile solvents.

(4) Bituminous substances, resins in combination with animal or vegetable fatty oils with or without mineral fillers and with or without pigments, and the addition of suitable volatile solvents.

The "resins" used may be common rosin, the damars, sandarac and Manilla, Kauri and Congo copals. These resins readily combine with the bituminous substances either by dissolving directly in the solvent or by first fluxing together.

Vegetable and animal fats improve the weathering power of a bituminous paint and therefore should be added in the rôle of a flux. The harder the bituminous base and the higher its m. p. the larger is the amount (%) of the fatty oil that can be incorporated into the admixture.

Fillers added must be of low specific gravity, finely powdered (they should pass through a 200-mesh sieve) and their function is to harden a paint and also to cheapen it.

The solvents used in the preparation of bituminous paints comprise the following classes :

1. *Petroleum Products*—gasoline, naphtha (benzine), white spirit, and kerosene and their sub-fractions. (White spirit is midway between the low flash, boiling point and solvent power of gasoline on the one hand and the higher flash, boiling point and solvent power of the kerosene.)

2. *Coal-tar Distillates*—in the order in which they distil benzols, toluols, xylols, solvent naphthas.

3. *Wood Solvents*—acetone oils, light wood oil, heavy wood oil (creosote), wood turpentine, pine oil, rosin spirits and rosin oil.

4. *Manufactured Chemical Solvents*—comprising carbon disulphide, carbon tetrachloride and the non-inflammable chloro-compounds such as $C_2H_2Cl_4$, etc.

The comparative volatilities of some of the commercial solvents generally used in bituminous paint manufacture are for 2 c.c. of each solvent evaporated under identical conditions from a metal surface $3\frac{1}{2}$ in. square, according to Abraham, as follows :

CS_2	$3\frac{1}{2}$ mins.	Turpentine	142 mins.
CCl_4	$4\frac{1}{2}$ "	Wood turpentine	480 "
90% benzol	$13\frac{1}{2}$ "	80° gasoline	4 "
50% benzol	23 "	66° benzine	16 "
Commercial toluol	33 "	Kerosene	475 "
Solvent naphtha	107 "		

The proportion of solvent used depends on (1) the nature of the bituminous base, (2) the solvent capacity of the particular solvent used, (3) the consistency required to be possessed by the finished paint. Generally it varies in amount from 20% to 80%, a smaller percentage being used in heavily-loaded paints for masonry, and for sealing joints in compound sheet roofing.

Light-bodied paints containing a larger percentage of solvent are used when it is desired to secure great penetration, rapid drying properties or when the paint is for dipping purposes.

In general, the higher the susceptibility of the base the lower will be the viscosity of the resultant paint. Petroleum residual asphalts and the pitches from wood tar, water-gas tar, oil-gas tar, and coal tar will form paints of lower viscosity than those fluxed with asphaltites, blown petroleum asphalts and the non-susceptible fatty-acid pitches.

Tar pitches produced by the destructive distillation of bones, wood, lignite and coal tar are more difficultly soluble than asphaltic materials and rosin and fatty-acid pitches. Tar pitches dissolve most readily in the following solvents, and in the order enumerated, carbon disulphide, coal-tar distillates, and resinous wood distillates. Of the other pitches, rosin pitch, fatty-acid pitches, bone-tar pitch and lignite pitch are the most soluble, whilst oil-gas-tar pitch, water-gas-tar pitch, wood-tar pitch and coal-tar pitch are the least soluble.

Dissolved in coal-tar naphtha, natural asphalts and such residual asphalts as those from Texas and Mexican Petroleum, produce excellent paints for the preservation of metal and outside iron and steelwork, and these paints will withstand dampness and all forms of chemical fumes and vapours. They are generally elastic and do not chip.

In a review of recent large-scale tests relative to the protection of metal surfaces, H. A. Gardner²¹⁰ mentions the wide use of bituminous coatings, which are often made by blending refined coal-tar pitch, asphalt, linseed oil, and oleo-resinous varnishes, subsequently thinning down with turpentine or light mineral thinner. When coal tar is used in the manufacture of paints, it should be refined. Ammonia and water in the tar are the active causes of non-adherence to metal. The presence of large quantities of free carbon or naphthalene in the tar will cause disintegration. For refining, the crude tar may be heated to approximately 115° C., holding it at that temperature until the water is evaporated. From 5 to 10% of lime may be stirred in, in order to neutralise the

free acids. The tar may then be thinned with benzol or mineral spirits. If a rapid-drying paint is desired, a quantity of resinous varnish may be added. The addition of Chinese wood oil and asbestine in a coal-tar paint made along the above lines will aid in producing a film that is not so subject to "alligatoring" when exposed to the sun. However, none of these paints is as durable as a linseed-oil paint when exposed to the sun. Bituminous paints of the above composition are used as coatings upon pipe-lines in acid factories, tanks containing dilute acids, metal submerged in water, and for other similar work. For such purposes it is generally advisable first to coat the metal with a thoroughly hard-drying prime coating, made by adding $\frac{1}{4}$ lb. of litharge to a gallon of prepared red lead or other rust-inhibitive paint. The bituminous paint may then be applied. Steel mine timbers subjected to sulphur water and gas, reservoir tanks containing water, submerged lock gates, tunnel metal, etc., may be efficiently preserved from corrosion by this method.

Jellying of Asphalt Paints.

In asphalt paints containing as part of the bituminous base fatty-acid pitch, bone-tar pitch, rosin pitch or any other pitch in which fatty acids or other similar acids are present, care is needed in the choice of a pigment in those cases where the addition of pigment is essential or desirable. Such pigments as chrome-green, chrome-yellow, zinc oxide, *i.e.*, those containing a metallic base, react with free fatty acids and rosin acids to form insoluble soaps and cause a certain amount of solidification known as "gelatinisation," "jellying" or "livering" of the paints. In a recent contribution to the discussion of this subject F. Singleton²¹¹ contends that the presence of water is an essential auxiliary factor in causing "livering" or thickening.

Furthermore, a paint which jellies slowly in an unrefined solvent will jelly more rapidly in the same solvent after the latter has been subjected to acid and alkali refining. A thin paint on jellying will precipitate and remain as two layers. Thicker paints may settle out, but the incrustation of the layers so increases that in time the two layers may appear homogeneous.

Recently the subject has received attention at the hands of H. C. Fisher,²¹² who has found that sulphuric acid will cause asphalt paints to jelly, whether it is added to the base before dissolving, to the solvent before dissolving the base in it, or to the finished paint whether hot or cold. The rate of jellying appears to be

proportional to the amount of sulphuric acid present. Under certain conditions such substances as caustic soda (NaOH) or sodium sulphate will cause thickening of asphalt paints. In the case of steam blowing of asphalts to remove sulphur compounds, some of these latter may give rise to sulphur dioxide and ultimately to sulphuric acid.

The rate of jellying of paints made from air-blown petroleum asphalts is dependent on the nature and composition of the bituminous ingredient and on the solvent used. A petroleum residual asphalt blown with air in contact with lime (CaO) jellies extremely slowly, when contrasted with the same material not blown in contact with lime.

Furthermore, bituminous bases that are hard and at the same time possess tough and rubber-like properties (*i.e.*, low susceptibility factor, considerable elasticity, resilience and tenacity) when used alone are apt to gelatinise after solution in the volatile solvent. This is particularly the case with hard, rubbery, fatty-acid pitches, such as those from cotton black grease distillation and wurtzilite asphalt. The underlying causes in these cases are more obscure and uncertain than in the case of paints where there is possibility of the formation of insoluble soaps.

In an account of the use of bauxite as a refining agent for petroleum distillation by A. E. Dunstan, F. B. Thole and F. G. P. Remfry ²¹³ mention is made of bauxite as a polymerising agent, polymerisation of unsaturated hydrocarbons largely present in cracked spirit taking place in contact with the bauxite resulting in the formation of gums of high molecular weight and boiling point. Two methods of refining such cracked spirit are available. In one of these the gumming polymers are washed out of the bauxite and in the subsequent distillation remain in the still, and a non-gumming distillate results. From the aspect of asphalt paints and their liability to jellying the importance of removing these polymers from bauxite-refined kerosene and white spirit is apparent.

Black Japans.—The term “Japan” is intended to define the dark-coloured menstruum which is applied to the surface of metals, wood, or other fabric and subsequently hardened by baking. The japans are used mainly in high-class coach work, and the specific purpose of black japans is the production of a brownish-black ground of a particular translucence appearing as though their colour were reflected from an under surface; in this respect the japans differ from such pigmented preparations as black enamels, which appear to reflect colour from the surface only.

The base of cheap japans is solely a bituminous material, but the highest grades contain, in addition, a vegetable drying oil with or without the addition of some gum resin, and according to the nature of the ingredients and the method of treatment the japans may vary from an opaque black to a translucent brown—but all are extremely hard, tough and resistant to abrasion.

The bituminous materials used are solid and semi-solid native asphalts, such as the purest forms of gilsonite, Barbados and Trinidad manjak, and in some cases residual asphalts from aromatic-base petroleums having the property of hardening on baking. Toughness may be imparted by fluxing with a small percentage of blown petroleum asphalt or fatty-acid pitch. Fatty-acid pitches, which have been overheated in the course of manufacture and have thus lost their more volatile constituents, and become partly polymerised, are particularly useful in the preparation of black japans, even to the extent of being used without further admixture.

Bituminous materials for use in the manufacture of japans must fulfil the following requirements :

1. They must be homogeneous and free from mineral matter, particularly any of a gritty nature.
2. They should be opaque and have a black streak.
3. They should possess a distinct conchoidal fracture and brilliant lustre, should not flow or lose their shape and should retain sharpness of angles even when immersed in boiling water.
4. They must not separate, curdle or gelatinise on thinning with petroleum naphtha.
5. They must bake in a reasonable time to a tough, permanently glossy coating without shrivelling or "crazing."

Gilsonite and such glance pitches as manjak will blend with fatty-acid pitch, and the resulting mixture can be thinned with petroleum naphtha to brushing consistency. But a tougher and more elastic japan may be prepared by incorporating a proportion of thickened linseed oil, and incidentally the gloss is improved. Semi-drying oils, which will oxidise to tough coatings at elevated temperature, may be substituted for linseed oil, especially if boiled and combined with driers.

Semi-glossy and flat black japans are prepared by grinding carbon black into the foregoing mixtures; the resulting baked surface then has an appearance resembling hard rubber.

Japans are applied to surfaces by dipping, spraying, flowing or

brushing, and where only a thin coating is required probably a mechanically-operated spraying appliance yields a more uniform surface than results from brushing. The coated surface is then heated in special japanning or stoving ovens for 1—4 hours at a temperature of 95—220° C., depending on the composition of the japan and the nature of the material being coated. Generally wooden and similarly slightly porous articles require more baking than metals, and modern practice resorts more to higher temperatures for shorter periods of time than to the converse.

As japans do not invariably possess a great degree of elasticity or weather resistance, the practice is resorted to of coating them with a suitable finishing varnish, as in coach japans, but generally it may be said that a baked japan forms a harder, tougher, and more weather-resistant coating than that of a bituminous varnish left to air-dry at room temperature.

The art of the varnish-maker consists in the preparation of a japan of great depth and intensity of colour without employing so high a proportion of pitch or suitable bituminous material that solubility of the latter in the resultant coat takes place, a condition manifesting itself, as Morrell²⁰⁸ indicates, by the appearance on the finished work of an undesirable greenish fluorescence—the “greening” of the japan.

As Morrell²⁰⁸ also points out, the shade is difficult to control: some japans yield a chestnut-black coloured film, due to the variety of pitch used. The latter should be as free as possible from volatile bodies likely to interfere with the lustre and to leave the film tacky. The coating should stand polishing the day following application. The following formulæ are quoted by Morrell²⁰⁸ as being very roughly representative:

	1.	2.
Hard gum	25	20
Natural or petroleum asphalt	8.4	20
Boiled oil	16.8	20
Turpentine	49.8	20

Attempts have been made to introduce aniline blacks in place of pitches to produce a more intense black, but the addition appears only to impair the drying power of the film.

Some japans consist of a bituminous base with boiled oil and a petroleum thinner, and thus approximate to the ordinary air-drying Brunswick-black type of varnish.

A type of japan termed a Black Stoving Enamel is prepared by incorporating a considerable amount of drying oil with the solid bituminous base, and is used for insulating armatures and field coils

of motors and dynamos. The armatures or coils are thoroughly dried in a suitable oven to remove all traces of moisture, and then dipped whilst hot into the cold japan, and subsequently baked for 8—12 hours, or even up to 24 hours, at about 85—95° C. The resulting hard-baked bituminous japan protects the cotton or other fibrous insulation wrapped round the coils from moisture and chemical fumes, and if properly prepared and baked will withstand currents of extremely high voltage. Such baking or stoving varnishes must not soften when applied to armatures, and to prevent brittleness, which would have a deleterious effect, it is advisable not to incorporate resin with the japan, owing to the tendency of resin to impart brittleness.

In search of the best type of coating for iron vessels used to hold acid plating solutions, Andés²¹⁴ found an enamel varnish somewhat similar to a japan by reason of composition and method of preparation the most suitable on account of its elasticity, its behaviour in the bending test and resistance to blows. This asphalt stove varnish was made from gilsonite, a thickened linseed oil (stand oil) and tar. After application to the metal surface, the varnishes were stoved at from 100 to 135° C., a second coat being subsequently applied and dried in the same manner.

One of the defects to be countered in the preparation of baking japans is that of "pitting," and a variety of causes may operate to bring about this objectionable feature. H. Gardner and P. Holdt,²¹⁵ in a review of the causes of this trouble, submit a number of important points as follow :

Oils free from "foots" should be used; the bituminous materials selected must be free from mineral matter, and greasy, improperly ground carbon blacks, where pigments are required, should be avoided, whilst petroleum thinners of high boiling range and containing large amounts of non-volatile residues may be responsible for pitting and contraction of films.

Lack of cleanliness in the kettles and the containers for the japans—*i.e.*, contamination by residues of polymerised oils and various forms of varnish—must be avoided. The thinners to be used should be added slowly, otherwise separation of some components of the japans may occur, which are difficult to redissolve.

It is also recommended that surfaces to be japanned be free from grease and be chemically clean, in order to inhibit an unsatisfactory flow, and the japan should be applied warm to warm metal, the temperature in the japanning oven being raised gradually after the freshly-japanned articles have been placed therein.

The British Thomson Houston Co.²¹⁶ claim that a black japan can be made with water thinners by incorporating 5 gallons of japan base (asphaltic base and a drying oil) with 10 gallons of water containing half a gallon of ammonia solution (s.g. 0.9) and 10—20% by volume of a 20% solution of glue. Another proposal of a similar character involves the preparation of an emulsion of an asphalt oil base in water and the deposition of this base on the metal by means of an electric potential difference maintained in the bath containing the emulsion; the object to be japanned is made the anode, and if large should be pre-heated before immersion in the bath. Since the japan is deposited free from solvent, there is no resultant drip on conveying the japanned object to the baking oven.²¹⁷

More recently details are to hand of another method of making a japan in water solution.²¹⁸

Air-drying Black Enamels.

These are made in a manner analogous to that adopted for black japans, but materials of less carefully selected quality are chosen. Some contain only a pitch, boiled oil, and turpentine, and are of the Brunswick-black type, for which Morrell²⁰⁸ quotes the following representative formulæ :

(a) 45 lbs. of pitch, 6 gallons of boiled oil, and 6 lbs. of litharge, boiled until stringy and then cooled and thinned with 25 gallons of turpentine.

(b) 32 lbs. of gilsonite, 14 gallons of boiled oil, and 54 gallons of turpentine.

A quick air-drying black varnish for all sorts of iron work can be made by melting 28 lbs. of coal-tar pitch with 28 lbs. of a petroleum asphalt, and boiling for 8 hours, with subsequent addition of 8 gallons of boiled oil, which is incorporated by heat. After adding 10 lbs. of litharge and 10 lbs. of red lead, the mixture is boiled until the mass will set hard between the fingers. On cooling, the mixture is thinned with 20 gallons of turpentine. The varnish will dry in 1—2 hours. According to Morrell,²⁰⁸ the addition of small quantities of coal-tar spirit (cresylic acid) improves the solubility of the components of these black varnishes, but diminishes their drying power, and therefore is restricted to stoving black enamels.

Some idea of the requirements to be fulfilled by air-drying black enamels may be gathered from following British specifications extracted by permission of the British Engineering Standards Association from their Reports Nos. 2 X. 9, and 2 X. 10, respec-

tively, of Dec. 1920, official copies of which can be obtained from the Secretary of the Association, 28 Victoria Street, Westminster S.W. 1, price 2d. each, post free.

BRITISH ENGINEERING STANDARDS ASSOCIATION

British Standard Specification for Aircraft Material.

UNDERCOATING BITUMINOUS PAINT. (2 X. 9, 1920.)

1. *Description*.—The paint shall consist of a solution of high grade bitumen, and in addition to satisfying the clauses of this Specification, shall comply with the special requirements of Appendix II.

2. *Consistency*.—The paint shall be of such a consistency as will allow of easy application by brush or spray.

3. *Rate of Drying*.—The paint, when applied to a hard wood, shall dry at 70° F. (21° C.) in not more than 6 hours, to a glossy, smooth, hard surface, which does not become soft or tacky when the temperature is raised to 100° F. (38° C.).

4. *Elasticity*.—The film of the paint shall be tested for elasticity in accordance with Appendix I.

APPENDIX I.

Test for Elasticity.

The paint shall be applied to a panel of 30 S.W.G. tinned iron and allowed to dry in a nearly vertical position for 24 hours at 70° F. (21° C.). The panel shall be bent rapidly double over a $\frac{1}{4}$ in. diameter rod and straightened out again. The paint film shall show no sign of cracking at the point of bending.

APPENDIX II.

Special Test for Bituminous Paint.

Two coats of the paint shall be applied to a wood panel, and after remaining 16 hours in bright daylight, a coat of Wood Oil paint (B.S. Specification X. 16) shall be applied. The film of paint shall become dry after not more than 8 hours, and shall adhere to the bituminous undercoating.

BRITISH ENGINEERING STANDARDS ASSOCIATION

British Standard Specification for Aircraft Material.

AIR DRYING BLACK ENAMEL. (2 X. 10, 1920.)

(NOTE.—This material is to be used only for touching up Metal parts.)

1. *Description*.—The enamel shall be suitable for direct application by brush or spray. A single coat shall produce a complete covering.

2. *Rate of Drying*.—The enamel when applied to a metal surface shall dry at 70° F. (21° C.) in not more than 8 hours to a smooth glossy film.

3. *Elasticity and Adhesion*.—The film of the enamel shall be tested for elasticity and adhesion in accordance with Appendix I.

APPENDIX I.

Test for Elasticity and Adhesion.

The enamel shall be applied to a panel of 30 S.W.G. tinned iron and allowed to dry in a nearly vertical position for 48 hours at 70° F. (21° C.). The panel shall be bent rapidly double over a $\frac{1}{4}$ in. diameter rod and straightened out again. The enamel film shall show no signs of cracking at the point of bending and shall adhere to the metal surface.

A United States specification ²¹⁹ for a similar asphalt varnish is more detailed :

The varnish shall be composed of a high grade of asphalt, fluxed and blended with properly treated drying oils and thinned to the proper consistency with a volatile solvent. It must be resistant to air, light, lubricating oil, water and mineral acids of the concentration hereinafter specified, and must meet the following requirements :

Appearance.—Smooth and homogeneous; no livering or stringiness.

Colour.—Jet black.

Flash Point (closed cup).—Not below 30° C. (86° F.).

Action with Linseed Oil.—Varnish must mix freely to a homogeneous mixture with an equal volume of raw linseed oil.

Insoluble in Carbon Disulphide.—Not more than 1%.

Non-volatile Matter.—Not less than 40% by weight.

Fatty Matter.—Not less than 20% of the non-volatile. Must be liquid and not show any rosin by the Liebermann-Storch test.

Set to Touch.—Within 5 hours.

Dry Hard and Tough.—Within 24 hours.

Toughness.—Film on metal must withstand rapid bending over a rod 3 mm. ($\frac{1}{8}$ in.) in diameter.

Working Properties.—Varnish must have good brushing, flowing, covering and levelling properties.

Resistance to Water.—Dried film must withstand cold water for 18 hours.

Resistance to Oil.—Dried film must withstand lubricating oil for 6 hours.

Resistance to Mineral Acid.—Dried film must withstand action of the following acids for 6 hours: sulphuric acid, s.g. 1.3 (about 40% H_2SO_4); nitric acid, s.g. 1.22 (about 35% HNO_3); hydrochloric acid, s.g. 1.09 (about 18% HCl).

The original specification must be consulted for details as to the carrying out of these tests. Evidently the specification corresponds to that of an air-drying black enamel.

Various air-drying black enamels and varnishes are in use, their composition being suited somewhat to their uses and requirements. Such materials as Mexphalte, Patagonian asphaltum, Syrian asphaltum, etc., can be used without the addition of oils or driers. The asphaltum is melted slightly, then thinned down with 1—1½ times its weight of white petroleum spirit, turpentine or even coal-tar naphtha to brushing consistency. The resulting enamel dries in about an hour to a fine varnish-like gloss, which it retains. These enamels form excellent coatings for all classes of outside iron and steelwork, for fire grates and fenders, iron pipes, etc., being not only water-proof and rust-preventing, but non-conducting and insulating. The rapidity with which these black varnishes dry depends mainly on the volatility of the thinner used in their manufacture.

Insulating Varnishes.

Owing to their high dielectric constants, pitches are valuable insulating materials, and a solution of the pitch with gum or resin in a suitable thinner is allowed to impregnate the insulating material—paper, silk, cotton, etc.—and after volatilisation of the solvent, a film of non-conducting and moisture-resisting material is left. The varnish should have great penetrating power, and the dried film should be sufficiently elastic to withstand the strain due to bending and to temperature changes.

The functions of insulating varnishes are summarised by Morrell ²⁰⁸ as follows:

1. To provide a waterproof coating with sufficient elasticity to withstand the movement between parts produced either by rotation or by magnetic or electric forces.
2. To increase the insulating properties of the impregnated material.
3. To protect the parts from the action of oils and acids.

4. To prevent excessive rise in temperature through their relatively high thermal conductivity.

Insulating materials for treating paper and fabrics, and solid impregnating compounds have been dealt with in the previous chapter. Morrell²⁰⁸ quotes the following as typical of oil and pitch insulating varnishes for impregnating windings :

Stoving Black Insulating Varnish.

300	parts of thickened linseed oil
100	„ „ petroleum residual pitch
7	„ „ sulphur
2	„ „ litharge
1	part of manganese dioxide
100	parts of turpentine
400	„ „ light petroleum spirit

The conditions governing chemical action in high-voltage windings are given by Fleming and Johnson,²²⁰ who state that chemical action occurs only where air pockets are present due to imperfections in the windings, and then only when the voltage across them is high enough to produce a discharge. Oxidation then occurs in the air gap discharge, the effect on oils and gums being to produce organic acids, but asphalts and pitches are attacked only slightly, and paraffin wax not at all. The organic acids produced act in a strongly disintegrating manner on the varnish material.

In a review of the chemical problems arising in connection with insulating varnishes, H. C. P. Weber²²¹ mentions that varnishes give rise to acidic oxidation products (cf. volatile fatty acids) of low resistance, though this behaviour is not marked in the case of asphaltic varnishes. For impregnating, the penetration depends on the viscosity, body, and colloidal nature of the varnish—for binding, the strength and rigidity are important factors.

REFERENCES.

- ²¹⁰ Paint Manufacturers' Assoc. of U.S., Circular No. 202, 1924, pp. 302-327. ²¹¹ "Enamels," *Chemistry and Industry*, 1925, p. 25. ²¹² *J. Ind. Eng. Chem.*, 1924, **16**, 509. ²¹³ *J. Soc. Chem. Ind.*, 1924, **43**, 179T. ²¹⁴ *Farb. Zeitung*, 1923, 1260. ²¹⁵ Circular 145, Educational Bureau Scientific Section Paint Manufacturers' Assoc. of U.S., Feb., 1922. ²¹⁶ British Thomson Houston Co., English Patent 155,427 of 1919. ²¹⁷ *Chem. Trades Journ.*, 1920, May 15th. ²¹⁸ W. P. Davey and General Electric Co., U.S. Patent 1,472,716 of 1923. ²¹⁹ Circular No. 104, Bureau of Standards, U.S.A., 1920. ²²⁰ Fleming and Johnson, *Journ. Inst. Elect. Eng.*, **47**, No. 209. ²²¹ *Ind. Eng. Chem.*, 1925, **17**, 11.

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CHAPTER XXI

BITUMINOUS PAVING MATERIALS

Roadway and Pavement Construction—Surface Phenomena in connection with Asphalt Pavement Construction—The British Standard Specification for Tar and Pitch for Road Purposes.

As we have already noted in Chapter IX, the first asphalt block pavement of which any record is now extant was laid down by Nabopolassar (625—604 B.C.), the father of Nebuchadnezzar, but apparently the art was lost to mankind, for it was not until 1836 that asphalt was first used in London for foot pavements and in the United States in 1838, Seyssel asphalt from the Rhône Valley in France being the material employed. Later on we find asphalt roadways being constructed and Trinidad asphalt the material selected.

At the present day bituminous materials for constructing pavements, coating the surface of macadam, or for use merely as a means of dust-laying are finding increasing world-wide use, and all or any of the following materials, either singly or in combination, may be used, according to circumstances: native asphalts, residual asphalts, blown petroleum asphalts, asphaltites and the various tars and pitches, such as those derived from gas- and coke-oven works. Native asphalts are, however, the most used, and in 1921 the estimated annual consumption (world's) for paving was 669,000 tons.

It is not possible to dwell here on more than one or two interesting aspects of a study which rightly belongs to the domain of Highway and Pavement Engineering and Construction. It has been suggested, however, in certain quarters that asphalt is unsuitable for roadway construction on account of its tendency to yield a slippery surface. As the causes which produce this effect are known, their elimination is possible by suitable technical control, and it is worthy of note that out of 140 miles of arterial roads around London only some 20 miles are made with a concrete surface—the rest have an asphalt surface. At the present day, an elastic or resilient surface is considered as the ultimate solution of the road problem, this being the only surface capable of withstanding the pounding action of modern traffic with its heavy loads and high speeds.²²² In this respect, bitumen, according to its advocates, stands unchallenged—it offers great resistance to the effects of dampness and retains its smoothness of surface for many years.

Undoubtedly, the peculiar properties of Trinidad asphalt are due to the colloidal suspension of clay present. This is not deposited from solutions of the bitumen, even after standing for years. It is owing to the presence of this colloidal clay, together with sulphur

derivatives in the Trinidad asphalt, and to the sulphur derivatives in Bermudez asphalt, that these materials are so desirable in roadway construction, for asphalt serves the purpose of cementing together the mineral aggregates and sands used in laying the different types of pavements and road surfaces. It is worthy of note that the Thames Embankment is a type of Trinidad sheet asphalt pavement laid on old macadam and Trinidad asphalt concrete.

The surface of an asphalt pavement being an agglomeration of sand graded in size with a fine mineral dust and a bitumen in the form of asphalt of approved consistency, C. Richardson ²²³ regards the asphalt pavement as a heterogeneous system of two components, one a solid (the mineral aggregate) and the other a liquid (the bitumen).

The importance of surface phenomena and the relationship of solids in colloidal suspension to the liquids with which they are associated is definitely recognised in this connection, and has led to investigations on the properties of mixtures of colloidal clay and petroleum residual pitches with a view to their use in pavement construction. This aspect of the subject opens up a very fruitful field for investigation.

Already much work has been done in this direction in the manufacture of bituminous emulsions, and amongst the materials which have been used to form emulsions of the dust-laying oils and the more solid and semi-solid bitumens may be mentioned: soaps, those consisting largely of ammonium oleate being the most favoured; the alkalies, when used with tars and pitches, containing phenolic bodies; colloidal clays and mineral matters; small amounts of colloidal vegetable substances such as the saponins and vegetable mucilages.

In the typical sheet asphalt roadway we have the following to consider in brief outline:

1. The Foundation or Base Course.

This may consist of a brick or block roadway and sometimes even of old macadam, but the most satisfactory foundation is probably 4 to 9 ins. thick of Portland cement concrete.

2. The Intermediate or Binder Course.

This may be either graded or ungraded coarse-aggregate bituminous concrete; broken stone is used, and this may be limestone or granite, and asphaltic cement.

3. Surface or Wearing Course.

This is composed of graded sand and an asphaltic cement.

Typical asphaltic cements prepared from Trinidad and Bermudez asphalts respectively test as follows :

	From Trinidad asphalt.	From Bermudez asphalt.
(Test 7) Specific gravity at 77° F.	1.26	1.07
(Test 9b) Penetration at 77° F.	65	65
(Test 9c) Consistency at 77° F.	7.9	8.0
(Test 10b) Ductility at 77° F.	21.5	17
(Test 15c) Fusing point (cube method)	148° F.	150° F.
(Test 16a) Volatile matter at 325° F. in 5 hrs.	2.5%	3.2%
(Test 19) Fixed carbon	6.1%	9.8%
(Test 21a) Soluble in carbon disulphide	65.7%	97.6%
(Test 21c) Mineral matter	29.5%	0.3%

From a chemical point of view we have already (Chapter XII) seen that all the more or less solid bitumens consist of "asphaltenes" which impart cohesiveness and supply body and stability, whilst the "petrolenes" are extremely sticky and of cement-like nature. A solid asphalt cement should contain not less than 15% of "asphaltenes" and not less than 70% of "petrolenes" to have the proper degree of stability and adhesiveness; the "petrolene" must be sufficiently sticky, otherwise the asphalt may not be suited as a cement.

H. Tindale¹⁶⁰ considers that the "asphaltenes" in road tars are their most desirable constituents, and if this contention be correct, it supplies additional confirmation of the fact that prepared horizontal retort tars are much more useful as road tars than those prepared from vertical retort tars, for the reasons already indicated by Wright,^{158a} viz., horizontal retort tars are less paraffinoid.

The requirements of British Standard Specifications of Tars, Pitches, Bitumens and Asphalts when used for road purposes may be gathered from the following, extracted by permission of the British Engineering Standards Association from their Report No. 76, 1916, official copies of which can be obtained from the Secretary of the Association, 28, Victoria Street, Westminster, S.W. 1, price 1s. 2d. each, post free.

BRITISH ENGINEERING STANDARDS ASSOCIATION.

BRITISH STANDARD NOMENCLATURE OF TARS, PITCHES, BITUMENS AND ASPHALTS WHEN USED FOR ROAD PURPOSES.

INTRODUCTORY REMARKS.

The materials now used by Road Engineers for binding together the stones and other mineral aggregate used to form road crusts and road surfaces may be conveniently divided into three groups. These are :—

1. The tars and pitches obtained by the destructive distillation of coal or similar substances.
2. The bitumens and asphalts which are found in nature, or are obtained artificially from asphaltic oils.
3. Chemical binders, including the Portland and natural cements which owe their cementing value as road binders to chemical action, and which are not dealt with in the present report.

Hitherto the term "bituminous material" has been loosely applied to tar products as well as to bitumens and asphalts, but the Committee have from the first considered that it was desirable from the Road Engineers' point of view to maintain a sharp line of demarcation between the two groups. The views put forward in correspondence from America and by American engineers of standing and experience have been carefully considered, but the Committee still adhere strongly to the view that the description "bituminous" should be applied only to the second group.

In this country the first group of road binders, the coal tars and pitches, have been in use for many years, and as the Road Board in 1911 issued Specifications for the tars, tar oils and pitches, which they recommended for road purposes, these materials have already to some extent been defined by those Specifications. The Road Board early in 1914 issued a second edition of these Specifications. Only two classes of tar, and one class of pitch are dealt with, and as these Specifications are of such recent date, the Committee recommend that they be adopted provisionally as the British Standard Specifications for Tars and Pitches used for Road Work.

The Committee find that the choice of names for the second group of road binders is a matter of some difficulty. This difficulty is increased by the fact that whilst it is desirable to obtain the concurrence of the American Engineers to the nomenclature and definitions which the Committee now propose, the adoption of the American nomenclature for the various materials composing this group would be liable to lead to confusion and misunderstanding in this country.

The Committee have been very anxious to secure uniformity with American practice, and have carefully and fully considered the definitions adopted by the American Society for Testing Materials and by the Committee of the American Society of Civil Engineers, put forward by the American corresponding members, but it is felt that the definitions now decided on are preferable from the Road Engineers' point of view, as they are based on those characteristics of the materials which can be most readily verified when employed for road making.

In accordance with this view, the Committee consider that it is desirable to make a sharp distinction between coal-tar and paraffin-oil derivatives on the one side, and native bituminous substances and asphaltic oil residues on the other, and they are therefore unable to accept the American definition of Bitumen which would include the coal tars.

DEFINITIONS.

FIRST GROUP.

TAR PRODUCTS (PRINCIPALLY COAL TAR AND PITCH).

Definition of Tar.

1. Tar is the matter (freed from water) condensed from the volatile products of the destructive distillation of hydro-carbon matter, whether this be contained in coal, wood, peat, oil, etc.

Prefix denoting source of origin or method of production.

2. A prefix such as "Coal," "Wood," "Peat," "Gas Works," "Blast Furnace," "Coke Oven," etc., must be added to the word "Tar" to indicate the source of origin or method of production.

Definition of Pitch.

3. Pitch is the solid or semi-solid residue from the partial evaporation of tar.

SECOND GROUP.

BITUMENS AND ASPHALTS.

Definition of Bitumen.

4. Bitumen is a generic term for a group of hydro-carbon products soluble in carbon disulphide, which either occur in nature or are obtained by the evaporation of asphaltic oils. The term shall not include residues from paraffin oils or coal-tar products.

NOTE.—Commercial materials may be described as BITUMEN if they contain not less than 98 per cent. of pure Bitumen as defined above.

Definition of Native Bitumen.

5. Native Bitumen is bitumen found in nature, carrying in suspension a variable proportion of mineral matter.

The term "Native Bitumen" shall not be applied to the residuals from the distillation of asphaltic oils.

Definition of Asphalt.

6. Asphalt is a road material consisting of a mixture of bitumen and finely graded mineral matter. The mineral matter may range from an impalpable powder up to material of such a size as will pass through a sieve having square holes of $\frac{1}{4}$ inch side.

Definition of Native or Rock Asphalt.

7. Native or Rock Asphalt is a rock which has been impregnated by nature with bitumen.

Prefixes denoting Source of Origin.

8. The Committee recommend that for convenience of identification prefixes denoting geographically the source of origin should be attached to each of the four terms defined above.

BRITISH STANDARD SPECIFICATION FOR

PITCH FOR ROAD PURPOSES.

(Based upon the Road Board Specification No. 6 and published with the approval of the Road Board.)

Standard Pitch for Road Purposes in the United Kingdom shall be specified as under:—

BRITISH STANDARD SPECIFICATION FOR PITCH.

General.

1. This pitch is suitable for pitch-grouting. See "Road Board General Directions for Pitch-Grouting."

Consistency.

2. The pitch is obtained of the required consistency most conveniently by running it off from tar stills in which the distillation of the tar has been stopped at the point at which the residual pitch will give a penetration of 70 (or such other penetration as may be specified to suit climatic or local conditions) when tested at 25° Centigrade (77° Fahrenheit) on a penetrometer. Harder pitch may be softened or cut back, in the still or in a mixer at the tar works, to the extent necessary for it to give this penetration, by the addition of tar oil of the grade specified below in Clauses 7 to 10.

Where pitch of the required consistency is not thus directly procurable, it may be prepared by softening commercial soft pitch, as specified below in Clauses 4 to 6, by the addition of tar oil as specified below in Clauses 7 to 10. In preparing the softened pitch in this manner the tar oil is added to the pitch in the manner described under "Instructions for Melting the Pitch" in the "Road Board General Directions for Surfacing with Pitch-Grouted Macadam," in such proportions that the resultant softened pitch will give a penetration of 70 (or such other penetration as may be specified to suit climatic or local conditions) when tested at 25° Centigrade (77° Fahrenheit) on a penetrometer, with a No. 2 needle weighted to 100 grammes for five seconds.

PREPARED PITCH FROM TAR DISTILLERIES.

General Characteristics.

3. Pitch which has been procured of the required consistency directly from a tar distillery needs only to be thoroughly melted in the pitch heaters or boilers, but as a precaution against burning, 1 to 2 per cent. of tar oil may advantageously be put into the boilers with the pitch.

Pitch which has been procured of the required consistency directly from a tar distillery shall not yield more than 4 per cent. of distillate below 270° Centigrade, or 518° Fahrenheit, on distillation as described below in Clause 5, and shall contain not less than 16 per cent. and not more than 28 per cent. of "free carbon," as defined below in Clause 6.

COMMERCIAL SOFT PITCH.

Source of Pitch.

4. The pitch shall be derived wholly from tar produced in the carbonization of coal, except that it may contain not more than 25 per cent. of pitch derived from tar produced in the manufacture of carburetted water gas.

Fractionation.

5. On distillation in a litre fractionating flask (a distillation flask without special fractionating column) one-half to two-thirds filled, the pitch shall yield the proportions by weight of distillates stated below; the temperatures of distillation being read on a thermometer of which the bulb is opposite the side tube of the flask:—

Below 270° Centigrade or 518° Fahrenheit, not more than 1 per cent. of distillate.

Between 270° and 315° Centigrade or 518° and 599° Fahrenheit, not less than 2 per cent. and not more than 5 per cent. of distillate.

Free Carbon.

6. The pitch shall contain not less than 18 per cent. and not more than 31 per cent. by weight of free carbon. The free carbon is to be determined by the weight of the residue after complete extraction of all matter soluble in benzol or disulphide of carbon. The extraction is best carried out in a Soxhlet or similar apparatus by disulphide of carbon followed by benzol.

TAR OIL.

Source of Tar Oil.

7. Tar oil to be used is preferably a filtered green or anthracene oil, and shall be derived wholly from tar produced in the carbonization of coal or from such tar mixed with not more than 25 per cent. of its volume of tar produced in the manufacture of carburetted water gas.

Specific Gravity.

8. The specific gravity of the tar oil at 20° Centigrade (68° Fahrenheit) shall lie between 1.065 and 1.085.

Freedom from Naphthalene and Anthracene.

9. The tar oil after standing for half an hour at 20° Centigrade (68° Fahrenheit) shall remain clear and free from solid matter (naphthalene, anthracene, etc.).

Fractionation.

10. The tar oil shall be commercially free from light oils and water. On distillation in a litre fractionating flask (a distillation flask without special fractionating column) one-half to two-thirds filled, the tar oil shall yield the proportions by weight of distillates stated below; the temperatures of distillation being read on a thermometer of which the bulb is opposite the side tube of the flask :—

Below 170° Centigrade or 338° Fahrenheit, not more than 1 per cent. of distillate (light oils and water, if any).

Below 270° Centigrade or 518° Fahrenheit, not more than 30 per cent. of distillate (middle oils, and light oils and water, if any).

Below 330° Centigrade or 626° Fahrenheit, not less than 95 per cent. of distillate (heavy oils, middle oils, and light oils and water, if any).

REFERENCES.

²²² Sir Courtauld Thomson, reported in *The Chemical Age*, April 4th, 1925, p. 329. ²²³ "The Colloidal State of Matter in its Relation to the Asphalt Paving Industry," 1917.

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APPENDIX I

THE following is reproduced by the courtesy of the Director of the U.S. Geological Survey, Department of the Interior, Washington, the information contained therein having only recently been made available.

CARBON BLACK PRODUCED FROM NATURAL GAS IN 1923

By G. B. RICHARDSON

Mineral Resources of the United States, 1923—Part II

(Pages 89-90)

Published September 29, 1924

The production of carbon black from natural gas in the United States in 1923 amounted to 138,262,648 lbs., an increase of 104% over the production in 1922. The increase resulted from the expansion of the industry that followed the greater demand in 1922 for carbon black by rubber companies. The number of producers of carbon black reporting to the Survey increased from 26 in 1922 to 47 in 1923, and the number of plants operated from 43 to 69. The operations resulted in over-production during the later part of 1923, as indicated by the quantity of stocks held in the hands of producers. Stocks increased from 2,434,547 lbs. on January 1, 1923, to 38,320,814 lbs. on December 31.

The production by States in 1923 as compared with that in 1922 is shown in the following table. Louisiana led all the States in the quantity of carbon black produced, as it has in the last three years, and its output of more than 101,000,000 lbs. shows an increase of 142% over its output in 1922. The production of Kentucky in 1923 increased 134%. The production of West Virginia, on the other hand, declined slightly. Texas joined the States producing carbon black in 1923. The production of Wyoming, Oklahoma, Montana, and Pennsylvania, which ranked in the order named, is grouped together to avoid revealing the operations of individual companies.

*Carbon Black produced from Natural Gas in the United States
in 1922-23.*

State.	Producers reporting.	Number of plants.	Quantity (lbs.)	Value at plant.		Estimated quantity of natural gas used (M c. ft.).	Average yield per M c. ft. (lbs.)
				Total.	Average (cents.)		
1922							
Louisiana	14	18	41,966,856	\$3,564,393	8-5	38,004,000	1-1
West Virginia	11	18	20,095,481	1,714,576	8-5	12,087,000	1-7
Kentucky	3	3	4,306,875	416,549	9-7	2,300,000	1-9
Oklahoma	1	1	1,425,917	124,100	8-7	1,238,000	1-2
Wyoming	1	1					
Montana	1	1					
Pennsylvania	1	1					
	a 26	43	67,795,129	5,819,618	8-6	53,629,000	1-3
1923							
Louisiana	29	35	101,398,881	8,415,566	8-3	82,974,000	1-2
West Virginia	11	20	20,038,415	1,983,385	9-9	13,722,000	1-5
Kentucky	6	6	10,058,887	758,091	7-5	5,906,000	1-7
Texas	3	3	2,633,013	183,306	7-0	2,136,000	1-2
Wyoming	2	2	4,133,452	351,718	8-5	4,358,000	0-9
Oklahoma	1	1					
Montana	1	1					
Pennsylvania	1	1					
	a 47	69	138,262,648	11,692,066	8-5	109,096,000	1-3

a In counting the total number of producers a producer operating in more than one State is counted only once.

*Summary of Statistics of Carbon Black from Natural Gas in
the United States, 1919-1923.*

	1919.	1920.	1921.	1922.	1923.
Number of producers	17	19	23	26	47
Number of plants	36	35	41	43	69
Quantity produced :					
Louisiana	14,024,606	18,565,498	31,003,615	41,966,856	101,398,881
West Virginia	29,925,614	26,659,469	25,073,000	20,095,481	20,038,415
Other States	8,106,721	6,096,925	3,689,700	5,732,792	16,825,352
Total	52,056,941	51,321,892	59,766,315	67,795,129	138,262,648
Value at plants :					
Total	3,816,040	4,032,286	5,445,878	5,819,618	11,692,066
Average per lb.	7-3	7-9	9-1	8-6	8-5
Estimated quantity of natural gas used,					
.....M c. ft.	49,896,000	40,599,000	50,565,000	53,629,000	109,096,000
Average yield per M c. ft.	1-0	1-3	1-2	1-3	1-3

APPENDIX II

MESSRS. SHELL-MEX LIMITED, London, through their Technical Department, have kindly supplied a detailed table showing the characteristics of their well-known grades of Mexphalte. This table should be studied in conjunction with Chapter XIV, on Petroleum Asphalts or Petroleum Residual Pitches: the manuscript was in the press when the table was furnished to the author, otherwise the information therein would have been incorporated in the text of Chapter XIV.

Properties of Various Grades of Mexphalte.

	"E" Grade.	"DX" Grade.	"B. 1" Grade.	"R. 1" Grade.	"R. 2" Grade.	Spramex.
Specific gravity at 60°F	1.035	1.036	1.041	1.039	1.038	1.028
Flash point—Cleveland Cup	over 500°F	over 500°F	over 500°F	over 500°F	224°C=435°F	232°C=450°F
Loss on heating, N.Y. oven, 5 hrs. at 325°F	negligible	negligible	negligible	negligible	negligible	0.36%
Sulphur	5.8%	5.5%	5.5%	4.8%	4.8%	5.5%
Asphaltenes	26.1%	30.3%	37.8%	39.2%	36.5%	16.7%
Soluble in CS ₂	99.8%	99.8%	99.7%	99.5%	99.6%	99.8%
Melting point (R. & B.)	55°C=131°F	68°C=154°F	112°C=234°F	135°C=275°F	97°C=207°F	39.5°C=104°F
Melting point (K. & S.)	40°C=104°F	53°C=127°F	97°C=207°F	120°C=248°F	82°C=180°F	24.5°C=76°F
Conradson coking test	25.4%	26.0%	38.5%	26.5%	25.6%	19%
Co-efficient of expansion per °C. approx.	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006
Penetration at 77°F ..	50	25	4	8	25	200
Ductility at 77°F ...	120+	10	nil	1	4	120+
Dielectric strength 1 mm. gap	+35,000 volts	+35,000 volts	+35,000 volts	+35,000 volts	+35,000 volts	+35,000 volts
Ash (mineral)	0.2%	0.2%	0.3%	0.2%	0.1%	0.2%
Volatile matter (Conradson values used) ..	74.6%	74%	61.5%	73.5%	74.4%	81%

APPENDIX III

THE statistics below have been kindly supplied to the author by the Department of Overseas Trade, London, S.W. 1.

Statement showing the imports, exports (domestic) and re-exports of the undermentioned articles into and from the United Kingdom during each of the years 1921, 1922 and 1923, and January to November 1924, so far as possible.

IMPORTS.	1921.		1922.		1923.		Jan. to Nov. : 1924.	
Total imports of :	Cwts.	£.	Cwts.	£.	Cwts.	£.	Cwts.	£.
Carbon blacks	49,320	200,350	77,606	278,384	118,159	513,297	Not available.	
Pitch :	Tons.		Tons.		Tons.		Tons.	£.
Coal-tar pitch.....	568	5,226	834	6,660	59,659	286,613	Not available.	
Other sorts	5,746	114,391	4,231	40,969	4,423	34,367		
Asphalt and bitumen	92,903	788,126	146,649	870,012	262,871	1,464,321	256,076	1,327,995
EXPORTS (produce and manufactures of the United Kingdom).								
Total exports of :	Cwts.	£.	Cwts.	£.	Cwts.	£.	Cwts.	£.
Carbon blacks	4,239	14,413	5,707	15,717	8,939	30,530	Not available.	
Pitch :	Tons.		Tons.		Tons.		Tons.	£.
Coal-tar pitch	304,235	1,805,794	424,691	1,543,291	414,224	2,527,016	276,493	1,218,462
Other sorts	1,190	24,978	4,154	45,566	13,130	100,869	Not available.	
Asphalt and bitumen	Not separately distinguished.							
RE-EXPORTS (foreign and colonial merchandise).								
Total re-exports of :	Cwts.	£.	Cwts.	£.	Cwts.	£.		
Carbon blacks	775	4,792	1,201	5,081	6,807	34,346	Information not available.	
Pitch :	Tons.		Tons.		Tons.			
Coal-tar pitch	1	13	38	943	37	630		
Other sorts	297	8,463	306	7,364	242	4,413		
Asphalt and bitumen	4,850	52,570	3,578	30,908	7,194	47,820		

Note.—As from the 1st April, 1923, the term "United Kingdom" refers to Great Britain and Northern Ireland only.

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